Variability of atmospheric particulate matter at an urban and a regional background in NE Iberian Peninsula

Research project / Treball de recerca

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Barcelona, September 2007

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1. SUMMARY

Atmospheric particulate matter (PM) is an important atmospheric pollutant constituted by solid or liquid particles emitted by a wide range of natural and anthropogenic sources. The effects of PM on human health, the climate and ecosystems have been widely studied. Epidemiological studies have shown a link between exposure to PM and adverse health effects such as respiratory or cardiovascular diseases. The influence of PM on climate on a global scale has also been proved. Efficient control and emission reduction strategies are essential in order to minimise the environmental and health impact of atmospheric pollution by PM.

PM_{10} and $PM_{2.5}$ levels at the Iberian Peninsula are characterized by a high mineral load when compared to Northern and Eastern European countries. This higher mineral contribution could be attributed to natural (African dust outbreaks and soil resuspension) and anthropogenic (road dust, demolition and construction) sources. African air masses loaded with mineral dust frequently reach the Iberian Peninsula increasing PM levels. This natural input may contribute to exceed the daily limit value established by the EU air quality directive for PM_{10} (50 $\mu gPM_{10}/m^3$, 1999/30/EC).

Data on levels and speciation of PM_1 in Europe are very scarce, especially in southern Europe. The results of the partitioning of PM components in the <1, 1-2.5, and 2.5-10 µm fractions in the study area may help to yield further insight into the influence of mineral matter on the different PM grain size fractions, and to provide evidence of possible interactions of mineral matter with other pollutants (gaseous pollutants and secondary PM pollutants).

The European Air Quality Directive 1999/30/CE requires the monitoring of PM mass concentration (currently PM_{10}). However, atmospheric aerosol concentration can also be monitored as particle number. Variability of particle number concentration and PM levels do not necessarily behave in a similar manner. PM mass measurements do not allow the study of aerosol processes taking place in the ultrafine particle range. The measure of both parameters becomes necessary for a detailed study of different pollution sources.

The interpretation of the variability of PM levels and speciation simultaneously recorded at a regional and an urban background site in the same area can support the identification of the external and local contributions for the implementation of plans for the improvement of air quality. The PM monitoring sites selected for this study are an urban background station under the influence of road traffic emissions from one of the largest avenues at the western edge of Barcelona and a regional background PM monitoring site in Montseny Natural Park at a distance of 40 km to the north-west of Barcelona. The levels and chemical speciation of PM were measured from 2003 to 2007 in Barcelona and from 2002 to 2006 in Montseny, with special interest on mineral matter. PM_{10}, $PM_{2.5}$ and PM_1 levels were measured continuously by means of a Grimm laser spectrometer dust monitor in both sites. 24 hour PM samples were collected on quartz micro-fibre filters with high volume samplers and analyzed for chemical speciation (PM_{10}, $PM_{2.5}$ and PM_1 in Barcelona and PM_{10} and $PM_{2.5}$ in Montseny). Furthermore, PM 1999-2001 data from other urban background sites in Barcelona were also used to support interpretations. The particle number concentration (in the ranges 13-800 nm in 2004 and 3nm-3µm from July 2005) was measured in Barcelona from 2004 by means of condensation particle counters (CPC). The possible influence of African dust outbreaks was investigated by means of air mass-back trajectory analysis using the Hysplit model and the information supplied by different dust maps and satellite images.

The mean annual PM levels measured at Montseny and Barcelona are considered relatively high when compared with the levels obtained in other rural and urban backgrounds around Spain and Europe. We can consider this difference associated to anthropogenic emissions as the area of study is very industrialized and populated.

The results obtained show that the annual variation of PM levels is highly influenced by the climatology and the frequency of African dust episodes in a year. Temporal changes in anthropogenic emissions, such as road traffic and industrial emissions also influence decisively the mean annual PM levels. In Barcelona although mean annual levels of PM_{10} do not follow a definite trend, those of $PM_{2.5}$ and PM_1 tend to increase from 1999 to 2006, suggesting an anthropogenic origin. Nevertheless the lower PM levels obtained during 2007 suggest that PM variation is due in part to meteorological causes. Conversely, at the Montseny site PM levels follow a decreasing trend from 2002 to 2007, probably attributed to climatology, but this trend could also be caused by a variation of the anthropogenic regional load because of changes in the industrial emissions in the region.

The contribution of African dust to annual PM levels depends on the frequency and intensity of African dust episodes in a year. In Barcelona, for the period 1999-2006, between 16-45% of the annual exceedances of the PM_{10} daily limit values were recorded during African dust outbreaks episodes, but not in all cases exclusively caused by the natural contribution. The remaining 55-84% of the annual exceedances can be attributed exclusively to anthropogenic causes. In Montseny the daily limit value was exceeded rarely and these exceedances can be attributed to the African dust contribution almost in all cases. PM mean annual levels at Montseny are very influenced by the winter pollution episodes occurring in the area but also by the frequency and intensity of African dust outbreaks in a year.

Results of PM speciation and size partitioning obtained at an urban site in Barcelona (Spain) show that the coarse fraction ($PM_{2.5-10}$) mainly consists of mineral dust (63%), sea spray (10%), and secondary inorganic aerosols (mostly Na, Ca, K, Mg sulphate and nitrate, 20-25%). The $PM_{1-2.5}$ fraction is made up of mineral dust (38%) and secondary inorganic aerosols (27%), with a fraction of carbonaceous matter (24%). The PM_1 fraction mainly comprises OM+EC (46%) with an important fraction of secondary inorganic aerosols (mostly ammonium nitrate and sulphate, 31%) and very minor proportions of mineral dust and sea spray. Thus, PM_1 contains a significantly lower proportion of crustal and marine components and a larger proportion of carbonaceous components than the $PM_{1-2.5}$ and $PM_{2.5-10}$ fractions.

The results show that the strategy of combining PM_{10} and PM_1 monitoring is a good tool for air quality monitoring across Europe. Thus, in PM_1 the dust load is considerably reduced when compared with PM_{10} and $PM_{2.5}$, and the measurement of PM_1 allows us to monitor levels of the same components (mostly carbonaceous and secondary inorganic components) in different scenarios. Simultaneously measured PM_{10} could also provide information on the levels of specific coarse components for a given site, such as mineral dust and sea salt. $PM_{2.5}$ represents an intermediate stage, with varying composition with the monitoring site and it may also be influenced by mineral dust.

In Montseny, the coarse fraction ($PM_{2.5-10}$) is mainly made up of mineral dust (81%), marine aerosol (9%) and nitrate (10%). The carbonaceous material, ammonia and sulphate are found at very low levels in this fraction. $PM_{2.5}$ is a mixture of SIA (40%), carbonaceous material (24%) and mineral dust (10%). The mass of marine aerosol (2%) and that of mineral dust are reduced in the $PM_{2.5}$ with respect to the PM_{10}. Almost

no OM+EC is present in the $PM_{2.5-10}$ fraction. Most sulphate is present in the fine fraction.

The results of comparing mineral dust contributions at Barcelona and Montseny show that most of the mineral load at the urban site has an anthropogenic origin, although it is accentuated by climate causes as low rainfall, with the consequent scarce washout of the road dust from streets.

The mean levels of particle number concentration registered in Barcelona were around 19.000 #/cm^3 and similar to those registered at other urban background sites in Europe. The study of the daily cycles of particle number concentration at Barcelona shows that traffic is the major source to particle number levels. The increase in the levels during traffic peak hours is related to the ultrafine particles emitted directly or formed by nucleation processes from gases emitted by vehicles. The decrease in particle number concentration when the traffic intensity diminishes is related to the coagulation and condensation processes of the ultrafine particles. The increase in particle number levels observed at noon, when solar radiation is maximum, is related to the formation of new ultrafine particles by photochemical nucleation processes.

2. INTRODUCTION

2.1. Atmospheric aerosols

Atmospheric particulate matter (PM) is defined as solid and/or liquid particles (with the exception of pure water) that enter in the atmosphere (Mészáros, 1999). Atmospheric particles are emitted by a wide variety of anthropogenic and natural sources. The nature of the source influences both the physical properties (e.g. mass, size, specific surface, density or number-density) and the chemical composition of the particles.

Various mechanisms give rise to the formation of atmospheric particles. *Primary particles* are emitted directly from the source to the atmosphere. *Secondary particles* are formed in the atmosphere after some chemical reactions from precursor gases (mainly sulphur dioxide, nitrogen oxides, ammonia and volatile organic compounds). The reactions to form secondary particles can be gas to particle conversions by homogeneous nucleation or heterogeneous reactions between gases and atmospheric particles to form new particles by coagulation or adsorption (Warneck, 1998).

Natural origin aerosols like windborne crustal material, sea spray, volcanic emissions, naturally caused biomass burning, biogenic emissions, secondary aerosols generated from gaseous natural precursors (SO_2, NO_X, COVs emitted by volcanoes, storms, soils and plants), spores or pollens are important sources of particulate matter in the troposphere. Between all possible sources of crustal material, the material from arid or semi-arid areas from latitudes between 10^oN and 35^oN in Northern Africa, Middle East and Central Asia represent the 44% of the contribution to the total mass of the atmospheric aerosol in our planet (Prospero et al., 2002). This material can be injected into the atmosphere when high temperatures and certain conditions of air mass circulation are presented.

Anthropogenic sources of aerosols are mainly due to road traffic (emission of precursor gases and ultrafine carbonaceous particles, brake and tyre wear and pavement erosion), fossil fuel combustion, energy plants, metallurgy and other industrial activities (mainly cement, ceramic and brick production), agricultural activities, waste treatment plants and fertilizer production plants. An important proportion of the anthropogenic aerosol is made up of secondary particles produced photochemically from

anthropogenic gaseous pollutants. The biomass burning oriented to obtain new land for agriculture purposes represents an important anthropogenic source.

The global planetary emissions of particulate matter to the atmosphere are summarized by IPCC (2001) as shown in Table 2.1. In a planetary scale natural primary emissions prevail. Conversely, anthropogenic emissions are a low proportion of the total, being mainly secondary. However, these proportions are very different considering PM origin at urban or industrial areas, where traffic and industrial emissions are the main sources of PM.

Table 2.1. PM emission in a global scale (IPCC, 2001).

PARTICULATE MATTER EMISSIONS (10^6 t/year)		
Primary particles	Mineral Sea spray OC EC Biomass burning Industry	1000 - 3000 1000 - 6000 55 - 200 10 - 17 45 - 80 40 - 130
SO_4^{2-}	Anthropogenic Biogenic Volcanic	69 - 214 18 - 118 9 - 48
NO_3^-	Anthropogenic Natural	9 - 19 9 - 18
Anthropogenic organic compounds		0.3 - 2
Biogenic volatile organic compounds		8 - 40

2.2. Aerosol size distribution

Atmospheric aerosols range in size from a few angstroms (Å) to some tens of micrometers. They can be classified by a series of size ranges, generally related to their formation mechanisms (Figure 2.1).

In accordance with **atmospheric sciences**, the *fine mode* includes particles <1µm (PM_1, Whitby, 1978; Wilson and Suh, 1997). This is due to the fact that most particles in the *coarse fraction* (>1µm) are primary and formed by mechanical processes (such as mineral dust and sea spray). Despite the predominance of the primary particles in the coarse mode, secondary particles may also be found (Wakamatsu et al., 1996, Querol et al., 1998). Such secondary particles are formed by chemical interaction of gases with primary particles of crustal or marine origin (most >1µm). In the *fine fraction* (PM_1)**,** the *nucleation mode* expands in the range <20nm and usually presents the

maximum number-density around 5-15 nm particle diameter. The origin of these particles with residence times (average time spent by the particles in the atmosphere) of a few hours is the condensation of gaseous precursors. The nucleation depends on factors as the concentration of the precursor gas, the temperature and the relative humidity (Seinfeld, 1998). *Aitken mode* particles range from 20 to 100nm and originate from either primary particles (such as diesel soot), or by growth of nucleation mode particles. The expression *ultrafine particles* is used mostly in health related literature as notion for particles less than 0.1 μm, thus covering nucleation mode and most of Aitken mode particles. The coarser mode of the fine PM fraction is the *accumulation mode* (0.1 to 1 μm). In the atmosphere Aitken mode particles grow to accumulation mode particles by coagulation or condensation of vapour on their surface. These particles have the longest residence time in the atmosphere.

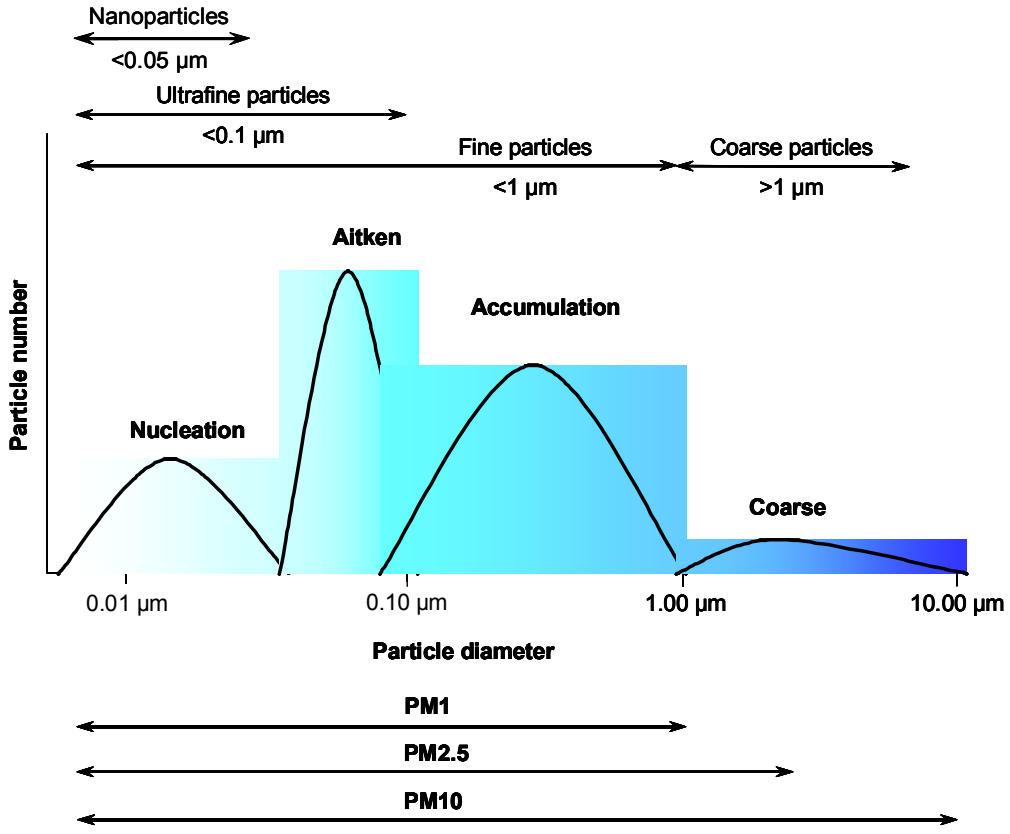

Figure 2.1. PM size distribution ranges (adapted from Viana, 2003).

According to **health sciences**, the PM fraction <100 μm (PM_{100}) is known as inhalable PM. The PM fraction <10 μm (PM_{10}) is known as the thoracic fraction since this is able to enter the thoracic airways. Finally, there is a finer size fraction (PM<4 μm or PM_4) that could penetrate the conductive airways of the tracheobronchial tree that distributes the inhaled air to the gas-exchange airways in the lungs. This fraction is known as respirable PM (see as an example US-NIOSH -National Institute for Occupational

Safety and Health, Centres for Disease Control and Prevention-guidelines). However, in **air quality** PM_{10} (defined as the mass fraction of PM that pass through a selective inlet for an aerodynamic diameter of 10 μm with a 50% efficiency) and $PM_{2.5}$ (PM <2.5 μm or alveolar fraction) are usually selected as monitoring parameters in worldwide environmental standards. Thus, in air quality, the coarse fraction is considered the one between 2.5 and 10 μm ($PM_{2.5-10}$), whereas $PM_{2.5}$ is considered the fine fraction. This particular size discrimination is the product of recognition that fine and coarse particles generally have distinct sources and formation mechanisms. However, as stated above, for the atmospheric scientific community these PM size ranges are not related to the formation mechanism. US-EPA (2004) states: 'Over the years, the terms fine and coarse, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage……. Fine particles and $PM_{2.5}$ are not equivalent terms.'

2.3. Aerosol composition

The major PM components are mineral dust, carbonaceous matter (organic and elemental carbon), sea spray, sulphate, nitrate, ammonium and water. The predominance of these chemical components in PM_{10}, $PM_{2.5}$ and PM_1 is linked to the prevailing emission sources and the formation mechanisms of the particles.

2.3.1. Mineral dust

The mineral matter is the major component of the total PM mass present in the atmosphere (44% of global planetary emissions, Duce, 1995; IPCC, 2001). However, on local or regional scales this proportion can be lower. These particles enter into the atmosphere by the action of winds on the surface of the Earth (Heintzenberg, 1994) and by crustal volcanic emissions. The major emission area is in the Northern Hemisphere, mainly the 'dust belt', an area with arid and semi-arid soils between latitudes 10 and 35ºN from western African coast to Middle East and Central and Southern Asia, where the mineral matter is resuspended (Prospero et al., 1999 and 2002). This mineral matter can be transported long distances by air masses. Other source of mineral PM is the resuspension of semi-arid soils. In the Southern Iberian Peninsula, in some areas with low precipitation rates and low vegetal cover, important resuspension processes with local or regional impact take place.

Natural mineral PM composition depends on the geology of the emission area. The major components are Al, Ca, Si, Fe, Ti, K and Mg. Other important trace elements are Co, Rb, Ba and Sr (Chester et al., 1996; Bonelli et al., 1996). The main mineral composition of PM is quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), clay minerals, mainly kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($K(Al,Mg)_3SiAl_{10}(OH)$), smectite ($(Na,Ca)Al_4(Si,Al)_8O_{20}(OH)_4 \cdot 2H_2O$ and palygorskite $(Mg,Al)_5(OH)_2[(Si,Al)_4O_{10}]_2 \cdot 8H_2O$, and feldspars like the microcline/orthoclase ($KAlSi_3O_8$) or the albite/anorthite $(Na,Ca)(AlSi)_4O_8$). In minor quantities calcium sulphate ($CaSO_4 \cdot 2H_2O$) and iron oxides (Fe_2O_3) can be found (Glaccum y Prospero, 1980; Ávila et al., 1997; Querol et al., 2002).

Although the main global contribution of mineral PM to the atmosphere has a natural origin, in urban and industrial areas the mineral fraction is mainly of an anthropic origin. Industrial activities, construction/demolition, mining activities, cement and ceramic production and smelters are typical anthropogenic mineral PM emission sources. Primary mineral particles associated to steel work and ceramic production sources can be fine particles. However, the majority of the sources of mineral matter emit coarse particles. An important proportion of these emissions is due to fugitive emissions by handling and transport of pulverulent material. Moreover, in urban areas, one of the principal sources of mineral matter (with construction and demolition) is the road pavement abrasion, brake and tyre wear by traffic. This mineral dust linked to traffic consists mainly of a mixture of mineral particles (pavement and dust deposited in the pavement, for example from demolition residues transported), carbonaceous particles (from tyres and traffic emissions deposited on the road) and metals (Fe, Cu, Sb, Ba from brakes, Ti, Rb, Sr from pavement, and Zn from tyres).

2.3.2. Marine aerosol

Marine aerosol (or sea spray) is the second more abundant component of PM emissions (38% of terrestrial global emissions, IPCC, 2001). However on a local/regional scale sea spray rarely exceeds 5% of the PM_{10} ambient air concentration. The sea spray concentrations at a given region depend on the geographic area, proximity to the coast and meteorology. Sea spray aerosols are mainly primary, generated by bubble bursting processes at the ocean surface or by the waves in coastal areas (Mészaros, 1999). They affect mainly the coarse fraction (the main part of the mass is present in the fraction bigger than 2.5 μm) and are constituted mainly by Cl^-, Na^+, SO_4^{2-}, Br^-, HCO_3^-, Mg^{2+}, Ca^{2+}, and K^+ (Mészáros, 1999). The major

component is NaCl (Warneck, 1988) followed by $MgCl_2$, Mg_2SO_4, or Na_2SO_4. In addition, there are secondary PM contributions constituted by sulphate produced by oxidation of the biogenic dimethyl sulphide (DMS). There are also trace elements like Al, Co, Cu, Fe, Mn, Pb, V and Zn (Seinfeld y Pandis, 1998; Mészáros, 1999). Some studies show that oceans are important sources of elements as Cu, V and Zn. Nriagu (1989) suggests that between 11 and 12% of natural Cu and V and 1% of natural Zn in the atmosphere comes from marine aerosol.

2.3.3. Carbonaceous compounds

Carbonaceous compounds represent around 2 to 5% of the global planetary emissions (IPCC, 2001). However, on a local/regional scale carbonaceous aerosols may account up to 20-40% of the ambient PM mass concentration. In urban areas it is one of the most abundant fractions of PM. An 80% of the carbonaceous species in urban and industrial areas is present in the finer fractions. The carbonaceous fraction of the particulate matter consists of both elemental and organic carbon. Elemental carbon (EC, black carbon, graphitic carbon or soot) is mainly primary and produced by the incomplete combustion of organic fuels. It is the compound with higher radiation absorption capability (Jacobson, 2001) and has a direct effect on the atmospheric radiative balance. The main sources are road traffic, (mainly diesel motors), power generation, specific industrial processes, biomass combustion and residential and domestic emissions

Particulate organic carbon (OC) is emitted directly or can result from atmospheric condensation of low-volatility organic gases emitted by similar sources to those of EC, like fossil fuels, biomass combustion and in a minor proportion agricultural emission sources and biogenic forest emissions that emit volatile compounds, precursors of secondary organic aerosols (SOA). The volatile hydrocarbons and other non-methane organic compounds are mostly of an anthropic origin, and they are important precursors of secondary organic aerosols. In urban areas these vapours are mainly emitted by fuel vaporization (fugitive emissions) and by combustion processes. Moreover, although in a smaller proportion, bio-aerosols (pollen, spores, microorganisms and vegetal or insect debris, among others) can contribute to increase the levels of primary organic carbonaceous aerosols. However, in urban and industrial areas anthropogenic sources of OC prevail (Rodríguez et al., 2002, Viana et al., 2006, Lonati et al., 2005).

2.3.4. Secondary inorganic compounds (SIC)

Sulphate, nitrate and ammonia are usually the major secondary inorganic compounds in PM. They are formed in the atmosphere from the precursor gases (SO_2, NH_3 and NO_X) through a gas-to-particle conversion. The secondary inorganic compounds represent around 5% of the global planetary emissions (IPCC, 2001). However on a local/regional scale can account up to 30-40% of the PM_{10} mass concentration.

Once the sulphur dioxide (SO_2) is emitted to the atmosphere (by industrial processes, energy generation, domestic and residential emissions and/or road traffic) its oxidation in the atmosphere gives rise to the formation of sulphuric acid aerosol, that will react later in the atmosphere to form particulate ammonium sulphate (by reaction with ammonia) and in a minor proportion calcium or sodium sulphate (by interaction with calcium carbonate and sodium chloride respectively). Both the sulphuric acid and the ammonium sulphate present a fine grain size (<1µm), whether the calcium and sodium sulphates present a coarse grain size (>1µm, Mildford and Davidson, 1987).

Nitrogen oxides (NO_X) are emitted mainly by traffic in urban areas and by electricity generation, industrial processes and domestic and residential emissions. These oxides are precursors of the atmospheric nitrate, originated from nitric acid (HNO_3), a product of NO_2 oxidation. Once the nitric acid is formed it can be neutralized and transformed in ammonium, sodium or calcium nitrate. The size distribution of particulate nitrate depends on the neutralizing agent of the nitric acid. Thus, ammonium nitrate presents mainly a fine grain size (<1µm), while the other two nitrate species are mainly in the coarse range. In cold and humid regions of Europe, nitrate aerosols are mainly fine in size, while in warmer and dryer regions, about 50% of the nitrate present in the PM10 fraction is in the coarse mode (Querol et al., 2004b, Putaud et al. 2004). The summer decrease of the nitrate levels in PM is remarkable in warm regions, as a consequence of the thermal instability of ammonium nitrate. Gaseous nitric acid predominates over particulate nitrate in this period of the year (Song et al., 2001; Wittig et al., 2004).

2.4. Aerosol lifetimes and removal processes

Particles are removed from the atmosphere by two mechanisms: deposition at the Earth's surface (dry deposition) and incorporation into cloud droplets during the formation of precipitation (wet deposition). Dry and wet deposition lead to relatively short residence times in the troposphere. Whereas atmospheric trace gases have

lifetimes ranging from less than a second to a century or more, residence times of particles in the troposphere vary only from a few days to a few weeks (Figure 2.2) Atmospheric aerosol lifetime depends on the diameter, chemical composition and thermodynamic properties of the particles.

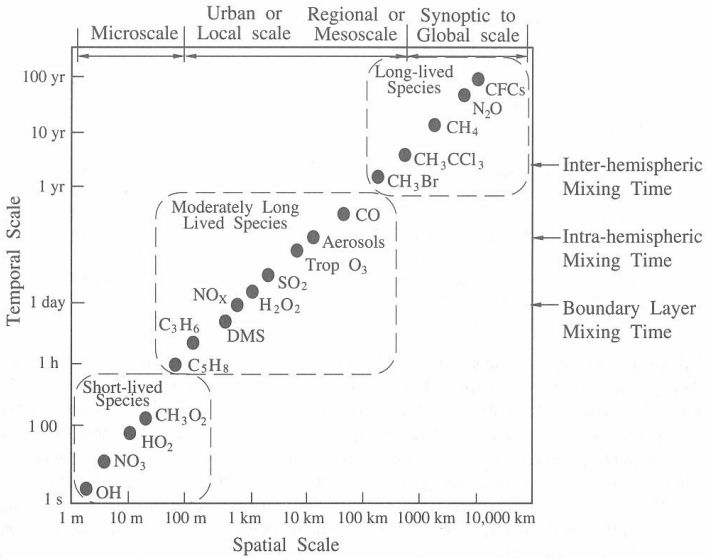

Figure 2.2. Atmospheric residence lifetime of some atmospheric components (Seinfeld and Pandis, 1998).

Nucleation mode particles (<20nm) lifetime is very short (hours) because of the fast conversion to Aitken particles. The lifetime of particles >50nm has an inverse relationship with particle size. Residence lifetime of coarse particles decreases when the diameter increases (hours for particles >20μm to 2-4 days for particles of 2-3μm diameter). Finally, accumulation mode particles and bigger Aitken particles (0.1-1μm) present the highest residence lifetime in the atmosphere (a few weeks, Mészáros, 1999).

Desert dust mineral particles are an exception. They present a mainly coarse grain size (>2.5μm) but there are also particles with diameters in the 0.1-1μm range that can be transported over 4000 km (Carlson y Prospero, 1972; Prospero, 1999). This is attributable to their transport on the free troposphere, although in areas near the emission source the boundary layer can also be affected. In the free troposphere the transport is favoured by a higher wind speed and a lower incidence of wet deposition processes (Prospero, 1999). Regarding the chemical composition, particle lifetimes are related to their hygroscopic characteristics. Accumulation and coarse particles are efficient condensation nuclei, since they usually have an important water soluble fraction, and they are mainly removed from the atmosphere by wet deposition. Carbonaceous particles (mainly EC) are more hydrophobic and need more time until surface oxidation allows wet deposition. However, an important fraction of OC is

hydrophilic. Carbonaceous particles lifetime is longer than soluble fraction particles lifetime (Pósfai y Molnár, 2000, Gaffney et al., 2002).

Finally, residence lifetime can also depend on thermodynamic properties. Solid/gas phase distribution of several chemical species depends on atmospheric conditions like temperature and relative humidity. This fact is especially important for ammonium nitrate and volatile organic compounds (Adams et al., 1999). Ammonium nitrate (NH_4NO_3) is not stable in particulate phase at a temperature higher than 20-25ºC (Stelson et al., 1979, Mészáros y Horváth, 1984, Willison et al., 1985, Seidl et al., 1996; Querol et al., 1998) and depending on the climatic region it can present a seasonal evolution in PM with winter maximums and summer minimums. A number of semivolatile organic compounds may also experience the same processes than NH_4NO_3. Conversely ammonium sulphate [$(NH_4)_2SO_4$] is stable and presents a long residence lifetime, being used as long distance transport tracer (Warneck, 1988; Seinfeld y Pandis, 1998; Mészáros, 1999).

In addition to the local and regional anthropogenic PM sources, both the levels and composition of ambient air PM depend on the climatology (mainly temperature, humidity, photochemistry, re-suspension of soil particles, rain scavenging potential, re-circulation of air masses, dispersive atmospheric conditions) and on the geography (mainly proximity to the coast, topography, soil cover and proximity to arid zones) of a given region. Different environmental conditions and PM source characteristics may account for different size partitioning of the PM components. Thus, the occurrence of a high load of PM mineral matter in dry regions may favour the interaction with gaseous pollutants and give rise to a high proportion of coarse secondary PM (Harrison and Pio, 1983; Mamane and Mehler, 1987; Wall et al., 1988, Querol et al., 1998) when compared with wet and cold regions. In a similar way, warm conditions may favour the partitioning of atmospheric pollutants towards the gaseous phases, which in turn may interact also with the coarse components and increase the secondary coarse PM load (Harrison and Kito, 1990; Wakamatsu et al., 1996).

2.5. Aerosol Measurement: Particle number and mass concentration

The concentration of atmospheric aerosol per unit volume of air can be expressed as mass (µg or ng/m^3), number (#/cm^3), surface (cm^2/cm^3) or volume (cm^3/cm^3) concentration (Figure 2.3). The particle grain size distribution is very different depending on the parameter represented.

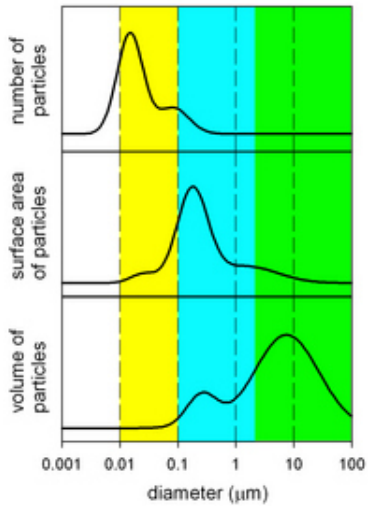

Figure 2.3. Particle number, surface and volume size distribution (Ultrafine Aerosols Research Group. National Centre for Atmospheric Research (NCAR), http://ua.acd.ucar.edu).

The European Air Quality Directive 1999/30/CE requires the monitoring of PM mass concentration (currently PM_{10}). However, atmospheric aerosol concentration can also be expressed as particle number, particle surface and particle volume concentration per air volume unit. Variability of particle number concentration and PM levels do not necessarily behave in a similar manner. In urban areas, the source that contributes in greater measure to levels of ultrafine particles and therefore to particle number is road traffic, while PM levels are highly influenced by the contributions of several sources. PM mass measurements do not allow the study of aerosol processes taking place in the ultrafine particle range. The measure of both parameters becomes necessary for a detailed study of different pollution sources. It has to be taken into account that high levels of PM are not equivalent to high levels of N and viceversa. Experimental measures of N and PM surface and volume concentrations are shown in Figure 2.4.

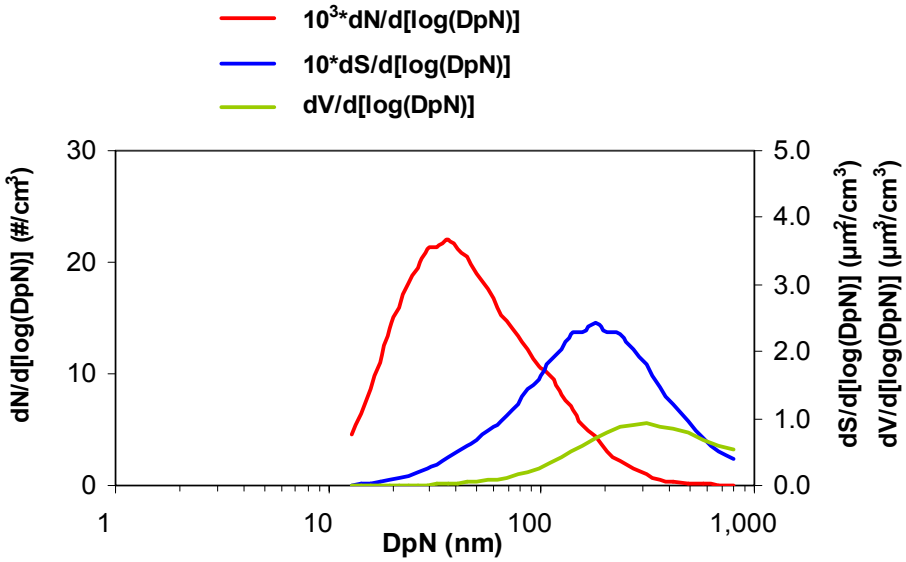

Figure 2.4. Experimental measures of number, surface and volume size distribution carried out by Jorge Pey in Barcelona (PhD thesis in progress).

Many epidemiological studies relate the direct exposure to high levels of ultrafine particles with an increase in mortality (Donaldson et al. 1998; Wichmann et al., 2000; Pope et al., 2002, 2004; Pope & Dockery, 2006). In this context, particle number is a more adequate parameter than mass concentration to monitor ultrafine particles.

In urban background areas, the source contributing in a highest proportion to increase N levels is road traffic. Primary particles (soot) are mostly emitted by diesel vehicles (Fraser et al., 2003; Brandenbergera et al., 2005). Secondary particles are formed by nucleation of precursor gases emitted by vehicles (Mathis et al., 2005, Rönkkö et al, 2006). Diesel emits primary carbon (mainly EC according to literature) particles but also secondary organic aerosols. A recent paper (Robinson et al., 2007) has shown that photo-oxidation of diesel emissions rapidly generates organic aerosol, greatly exceeding the contribution from known secondary organic-aerosol precursors, probably due to the oxidation of low volatility gas-phases species. This may account for the very low EC/OC ratios measured at Barcelona, even with a high diesel/gasoline cars rate. Both types of particles fall mostly in the size range <100 nm, and near emission sources are found in high concentrations (Morawska et al., 1998). During their residence time in the atmosphere and as the distance to the emission sources increases, the particles interact, coagulating and acting as nuclei where gaseous species like sulphate, nitrate and other organic compounds condense (Rose et al., 2006). As a result, particle sizes increase and particle number decreases. Therefore, it seems evident that in urban areas, particle number measurements reproduce to a large

extent road traffic emissions, being this parameter more adequate than mass concentration measurements to illustrate the impact of this emission source on air quality. However, in urban areas there is a big contribution of coarse particles to aerosol levels, but they have a higher impact on PM mass concentration and not very significant effects on number concentration levels.

There are other sources contributing to increase particle number. In forest areas, under specific temperature, insolation and relative humidity conditions, important nucleation episodes are reported (Boy and Kulmala, 2002, Mäkelä et al., 2000, Ketzel et al., 2004). Nucleation episodes in rural areas that reach particle number levels higher than the levels measured simultaneously in urban backgrounds are reported in rural background areas situated in areas with high anthropogenic activity (Rodríguez et al., 2005).

2.6. Aerosols and environment, climate and health

Aerosol particles have always been part of the atmosphere. As already mentioned, they are produced by natural sources such as crustal material, sea spray, volcanoes or fires. Other natural sources are condensable gases derived from oxidation products such as sulphur dioxide or biogenic emissions that form new nanometre-sized particles or condense on existing particles. Without particles in the atmosphere, there would be no rain, and the climate would be different (Mészarós, 1999; IPCC, 2001). Atmospheric composition has changed since human beings live on Earth. Nowadays, the largest fraction of directly emitted anthropogenic aerosol particles derive from combustion sources such as power plants, vehicles, or domestic stoves (Brimblecombe 2001). The amount of condensable gases has also changed due to the anthropogenic emission of sulphur dioxide and volatile organic compounds. Due to the world-wide industrialization in the last two centuries, the particulate air pollution in urban areas has drastically increased. Furthermore, due to long range transport, aerosol particles spread over thousands of kilometres and influence the earth radiation balance and the climate.

In addition to their influence on climate, atmospheric aerosols affect many aspects of human health and the environment. Aerosol mass and its toxic chemical components are known to have links to chronic respiratory and acute cardio-vascular problems. Aerosols are also closely linked to problems of visibility reduction, acid rain, and urban smog in many locations of the world.

2.6.1. Effects on health

The increases in mortality and morbidity during several mid twentieth-century air pollution episodes demonstrated to both scientists and governments that air pollution from heavy industry and residential coal combustion were hazards to public health (Brimblecombe 2001). Where governments introduced regulations to reduce emissions, the levels of ambient air pollution declined. Atmospheric particulate matter effects on health have been evaluated by means of epidemiological studies carried out since the 1980s proving that elevated aerosol mass concentrations are associated with an increase in mortality and other serious health effects (Pope and Dockery 1999; Pope et al. 2002 and 2004; WHO, 2003). Associations are reported between recent exposure and short term increases in mortality and morbidity from cardiovascular and respiratory diseases (Schwartz, 1996; Katsouyanni et al., 1997; Künzli, 2000). Many studies report that these health effects are strongly and consistently associated with small particles derived from combustion of fossil fuels, which are the particles that can reach the alveolar region of the lungs (Figure 2.5; Schwartz et al., 2000; Dockery, 2001; Dockery and Stone, 2007). The literature suggests that a range of health effects occur at PM levels below US and European regulatory standards. Elevated number concentrations of ultrafine aerosol particles <100 nm showed also an increased risk in mortality and morbidity in epidemiological studies (Seaton et al. 1995; Hoek et al. 2002; Miller et al., 2007; Pope and Dockery, 2006). Specific components such as soot, certain organics, or metals are believed to increase the risk of diseases (Jacobson, 2001; Kampa and Castanas, 2007). Especially, very young and elderly people are risk groups.

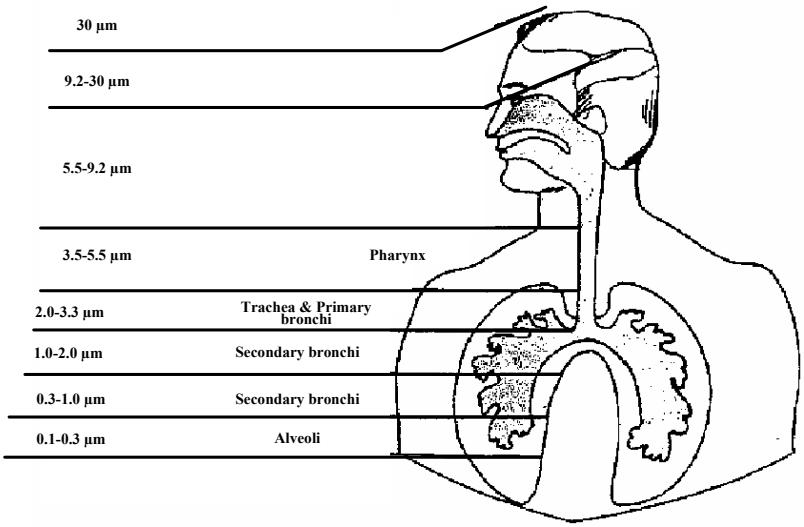

Figure 2.5. Particle sizes that affect the different parts of the human respiratory system. (http://www.epa.gov).

2.6.2. Effects on climate

Aerosols play a very important role on Earth's radiative balance. Aerosols influence the atmospheric energy budget through direct and indirect radiative effects (Levin et al., 1996; IPCC, 2001; Arimoto, 2001; Harrison et al. 2001; Ramanathan et al., 2001).

Aerosol particles scatter and absorb solar radiation depending on their chemical composition or refractive index. A fraction of the solar radiation is scattered back to space leading to a cooling effect. Another fraction of the solar radiation is absorbed by the particles leading to warming effect. These effects are called direct aerosol forcing of climate. The direct effect depends strongly on the size distribution and the chemical composition of the aerosol (Adams et al. 2001). Carbonaceous particles (mainly EC) contribute in a very important way to atmospheric warming (Rose et al., 2006). Diesel vehicles contribute in a much more important way than gasoline vehicles to ultrafine particles emissions and therefore to global warming, emitting EC particles in the ultrafine range, between 30-130 nm (Morawska et al., 1998; Zhu et al., 2002).

Aerosol particles act as nuclei for cloud and fog formation. Cloud (and fog) droplets scatter and absorb also solar radiation depending on the size and amount of incorporated absorbing material, respectively. Aerosol particles induce modifications of the cloud albedo, the droplet concentration number, the lifetime of clouds and the frequency of the precipitation. These effects are called indirect aerosol forcing of climate (IPCC, 2001). The size distribution (number and size) of cloud droplets strongly depends on the number size distribution of the aerosol. An increase in aerosol number concentration tends to increase the cloud condensation nuclei (CCN) which in turn, leads to increased cloud albedo and to changes in the Earth's radiation budget (Levin et al. 1996).There is also a semi-direct effect caused by the absorption of radiation by soots, locally lowering the cloud cover (Ackerman et al, 2000).

Cloud lifetimes and precipitation frequencies can also be affected, altering the hydrological cycle and water supply (Ramanathan et al., 2001). Scientific evidence indicates that in regions with high anthropogenic aerosol concentrations, aerosol forcing is of the same magnitude, but opposite in sign to the combined effect of all greenhouse gases (IPCC, 2001). Furthermore uncertainties are great. IPCC (2001 and 2007) estimates the average direct radiative forcing, through scattering of incoming radiation for sulphate, biomass and fossil fuel black carbon aerosols and the indirect forcing, through cloud condensation nuclei effects for all aerosols (Figures 2.6 and 2.7). Long-term monitoring of chemical properties of aerosols will be crucial to determine the

role that aerosols play in climate, to document changes in the regional air quality and to provide a scientific basis for policy decisions regarding control strategies.

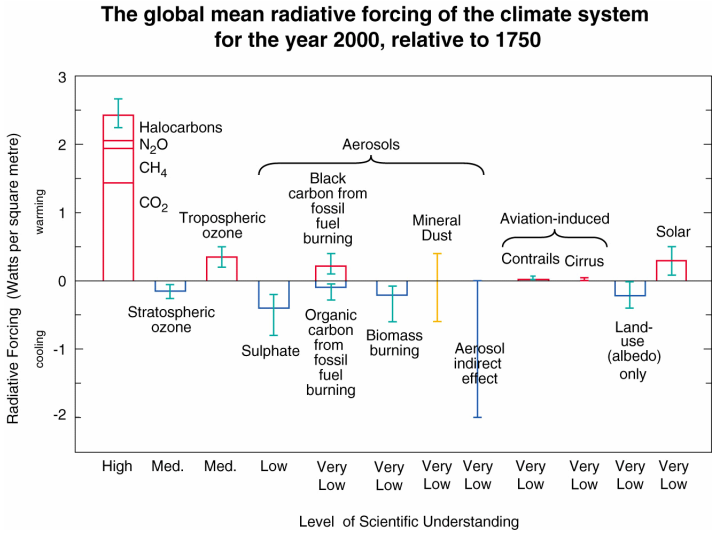

Figure 2.6. Global Mean radiative forcing estimations (IPCC, 2001).

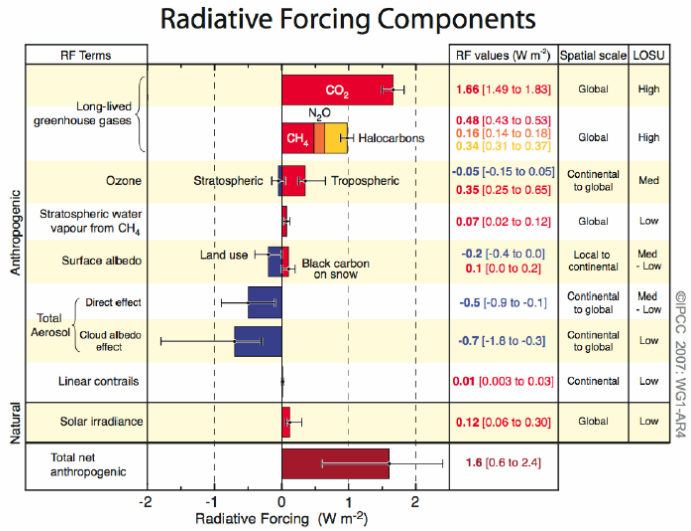

Figure 2.7. Global-average radiative forcing (RF) estimates and ranges in 2005 for anthropogenic CO_2, CH_4, N_2O and other important agents and mechanisms, together with the typical spatial scale of the forcing and the assessed level of scientific understanding (LOSU). The net anthropogenic radiative forcing and its range are also shown. Additional forcing factors not included here are considered to have a very low LOSU. Volcanic aerosols are not included in this figure due to their episodic nature (IPCC, 2007).

The quantification of aerosol radiative forcing is more complex than the quantification of radiative forcing by greenhouse gases because aerosol mass and particle number concentrations are highly variable in space and time (IPCC, 2001). This variability is largely due to the much shorter atmospheric lifetime of aerosols compared with the important greenhouse gases. Spatially and temporally resolved information on the atmospheric burden and radiative properties of aerosols is needed to estimate radiative

forcing. Important parameters are size distribution, change in size with relative humidity, complex refractive index, and solubility of aerosol particles. Estimating radiative forcing also requires an ability to distinguish natural and anthropogenic aerosols (IPCC, 2001).

2.6.3. Effects on ecosystems

Atmospheric particles can directly interact with ecosystems, like dust deposition on plant leaves or modification of the mineral content in waters, producing several effects.
The wet deposition of atmospheric particles, when acid species are incorporated to rain drops produces the phenomena known as acid rain. Aerosols and gaseous pollutants that produce acid rain can be natural (like SO_2 derived from volcanic eruptions or CO_2 emitted in forest fires) or anthropogenic (caused by the emission of pollutants derived from the use of fossil fuels). Acid rain has been studied from the 1970s (Likens, 1974 and 1989; Butler and Likens, 1991), showing that the acidification of ecosystems disturbs their operation. In lakes and oceans, this acidification of the environment can produce a modification of the life conditions of the species and even their death. Moreover, the deposition of nitrate and ammonia can contribute to the eutrofization of lands, lakes and surface waters. The atmospheric particle deposition on the Earth surface and surface waters can also alter the composition of underground waters (Wright, 1995). In the land, acid rain reacts with soil nutrients preventing their absorption by plants and dissolves toxic metals facilitating their absorption and producing damages even perceptible on the surface. Atmospheric particulate matter produces also damages on plants because of the deposition of particles on the leaves, affecting their capability to perform the photosynthesis (Emberson et al.,2003). This effect gives rise to important economical losses because of crop ruin
Atmospheric mineral dust transported from arid areas over long distances has also important effects on the biogeochemistry of land, surface waters and oceans as it represents and important source of primary nutrients like calcium, iron, nitrogen, potassium and phosphor (Prospero, 1999, Jickells, 2005).

2.6.4. Visibility reduction

Atmospheric aerosol determines the visibility in the atmosphere owing to the scattering and absorption of short-wave or visible solar radiation. In urban areas, anthropogenic atmospheric pollution can reduce visibility to a few meters. An urban environment usually has a visibility range from 10 to 100 km (WHO, 2002) and Horvath (1992)

calculated that the dispersion of solar radiation by air molecules produced a mean visibility of 337 km.

2.6.5. Degradation of building materials

In urban areas, atmospheric particulate matter deposition produces the degradation of construction materials exposed to the atmosphere, like cement and metallic structures of buildings and monuments, because of their interaction with the surface. This material degradation can also be produced by gaseous pollutants associated to particulate matter, such as SO_2 and NO_X (Alastuey, 1994 and Brimblecombe, 2003).

2.7. Current Environmental Standards and further regulations

Atmospheric particulate matter is monitored in air quality networks due to the above explained adverse health effects, its visibility reduction properties and its effects on climate. Until July 2001, in the Spanish regulation, the atmospheric particulate matter monitoring was performed by black smoke measurements and total suspended particles or TSP (Reales decretos 1613/1985, BOE no.219 from 12/9/85 and 1321/1992, BOE no.289 from 2/12/92), originating from the incorporation to Spanish regulation of the European Directives 80/779/CEE and 98/427/CEE. From July 2001, the European Directive 1999/30/CE comes into force and it establishes new air quality standards for atmospheric particulate matter. This new legislation changes the parameter to measure, from black smoke and TSP to PM_{10} and restricts the limit values permitted (Table 2.2). These standards are applied in two different periods of time. In the first phase (2005) the annual mean limit value is 40 $\mu g/m^3$ and the daily limit value is 50 $\mu g/m^3$ for the 90.4% percentile. The number of annual exceedances of the daily limit value permitted is 35 days. The second phase (2010) is more restrictive, with an annual mean limit value of 20 $\mu g/m^3$ and a daily limit of 50 $\mu g/m^3$ for the 99% percentile, corresponding to 7 days of exceedances permitted in a year. However, the Directive stated that the limit values fixed for the 2010 phase had to be ratified in the evaluation of the Directive in 2003 to come into force. This ratification was not approved so the first phase PM_{10} limit levels remained effective.

The directive also proposed to establish limit values for $PM_{2.5}$ by the end of 2003, as epidemiological studies associate more harmful health effects to smaller particles. An annual limit value in the range of 12-20 $\mu g/m^3$ and a daily limit value of 35 $\mu g/m^3$ for the

90% percentile were proposed, with 35 permitted exceedances of the daily limit in a year. However, the WHO exposes that the fraction 2.5-10 can also have an impact on health (WHO, 2003).

Table 2.2. Annual and daily limit values and permitted exceedances for the PM_{10} daily limit value, as established by the European Directive 1999/30/CE. Annual and daily limit values and permitted exceedances proposed for $PM_{2.5}$, as stated in the II Common Position on PM (EC, 2004). European Parliament and Council on Ambient Air Quality and Cleaner Air for Europe Directive Proposal (2006).

Reference parameter	Old directive 1992-2001 TSP	Directive 1999/30/CE			Directive Proposal 2006 $PM_{2.5}$
		Phase I 2005 PM_{10}	Phase II 2010 PM_{10}*	Suggested parameters* $PM_{2.5}$	
Target value (µg/m^3)					25 (2010)
Annual limit value (µg/m^3)	150	40	20*	12-20 (25)*	25 (2015)
Daily limit value (D.L.V.) (µg/m^3)	300	50	50*	35*	
D.L.V. permitted exceedances	18	35	7*	35*	
Exposure reduction objective from 2010 to 2020					20%**

* not in use as they have not been ratified in the evaluation of the directive.**PM2.5 Mean reduction in urban background sites from 2008-2010 to 2018-2020.

Regardless of the previous proposal, the EC is considering (according to the European Parliament and the Council on Ambient Air Quality and Cleaner Air for Europe Directive Proposal, draft from October 2006) the possibility to establish as definitive the PM_{10} limit levels for the phase I (2005) and to add an annual target value of 25 µg$PM_{2.5}$/m^3 in all the European territory (regional, urban and rural backgrounds, including hotspots) from 2010, that would become a limit value from 2015. Moreover, it intends to establish the Mean Exposure Indicator (IME) to a National level, an objective value for the progressive reduction of levels (exposure reduction) of $PM_{2.5}$ in urban sites. A 20% reduction of the mean levels in the 2018-2020 period, with respect to the levels measured in the period 2008-2010 is proposed for urban background sites in the Member States. Furthermore, the entry into force of the limit values of the phase II is definitively discarded.

Moreover, the 1999/30/CE Directive establishes criteria about micro and macro application of the monitoring stations, the number of sampling points and the measurement reference methods. Nevertheless, it does not establish this criterion strictly. The urban traffic sites must be located near roads with high traffic inside the cities to measure direct pollution of both the city and the traffic. Urban sites are located inside urban areas but in background areas that represent exposure level of citizens. Regional background sites are located in areas far from any direct anthropogenic

pollution source to get background measures at a regional and rural level. Finally, the industrial sites are located inside industrial areas to measure the local impact of an industrial area. Nevertheless, the criteria to classify the monitoring sites are not clear and the proportion of every type of site that should integrate an air quality network is not specified. This lack of precision in the micro-implantation allows that there are huge differences between Member states in the design of the air quality networks (http://air-climate.eionet.eu.int/databases). The new version of the Directive Proposal proposes to establish a maximum of 2 for the ratio between the number of urban background sites/hotspots from the Different Member states. In Europe there is a big difference between Spain, for example, with 80% industrial and traffic hotspots over the total and other member states, with 13% industrial and traffic hotspots over the total.

The directive 1999/30/EC recognises that exceedances of the PM_{10} daily limit levels can be caused by natural events. Natural events are *volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high wind events or the atmospheric resuspension or transport of natural particles from dry regions*. These exceedances can be discounted by the State Members after scientific validation (article 2.15 from the 1999/30/EC Directive). In Southern Europe, the natural episodes with the greatest impact on PM levels are the intrusions of African air masses, frequently with high dust loads (Querol et al., 1998; Rodriguez et al., 2001; Escudero et al., 2005; Gerasopoulos et al., 2006; Gobbi et al., 2007). The most common approach to quantify dust contributions is the study of PM chemical speciation (Rodriguez, 2002; Viana, 2003, Castillo, 2006). Escudero et al. (2007c) proposed a methodology for estimating the net dust load in PM_{10} during African dust outbreaks based on the analysis of time series of PM_{10} levels from regional background sites in Spain and quantifying the impact of African dust outbreaks on the levels of PM_{10} in air quality monitoring networks.

2.8. African dust outbreaks

Mineral dust particles enter into the atmosphere by the action of winds on the surface of the Earth (Heintzenberg, 1994) and then they can be transported long distances. The major emission area is in the Northern Hemisphere, mainly the *dust belt*, an area with arid and semi-arid soils between latitudes 10 and 35ºN from western African coast to Middle East and Central and Southern Asia (Prospero et al., 1999 and 2002). The low relative humidity (10%) and high summer temperatures (60-65ºC) in these areas are scenarios that favour the massive resuspension of particulate matter. The winds

and vertical convective air mass circulations over arid areas produce the resuspension to the atmosphere of the mineral particles that compose the desert soils (Dubief, 1973; Prospero et al,. 2002). Then, the nocturnal thermal inversion stability prevents the sedimentation of the particles injected into the atmosphere, forming the dust hazes typical of the Sahara and Sahel regions. Once resuspended, the mineral matter can be transported long distances by air masses (Carlson and Prospero (1972), Prospero and Carlson (1972), Prospero (1999), Duce (1995)). The circulation of dust masses from Northern Africa happens under different meteorological scenarios (Moulin et al., 2004; Escudero et al. 2005). The transport of mineral dust to the Iberian Peninsula can interfere in PM levels depending on the intensity of the event and the distance to the emission source. There are numerous studies that provide data about these processes on the North-eastern Iberian Peninsula (Martín-Vide and Moreno, 1985; Ávila et al., 1997, 1998, 1999; Díaz and Miranda, 1997; Rodríguez et al., 2001, 2002a and 2002b; Querol et al., 1998, 2001, 2002; Escudero et al., 2005 and 2007), where the impact of these events on PM levels and atmospheric deposition is exposed. African dust outbreaks can increment PM mean daily levels sporadically resulting in the exceedance of the established daily PM_{10} limit value but on an annual time scale this contribution does not produce an important increment in PM levels. The contribution of this kind of episodes to the PM annual means depends on the frequency and the intensity of the African dust outbreaks during the year.

Many studies have characterized the emission areas of mineral dust. The Sahara and Sahel deserts are the areas that produce a larger emission of dust particles to the atmosphere (Prospero et al., 2002). Various authors estimate the emission of particulate matter from Northern Africa arid areas to be between 560 and 760 t/year (D'Almeida, 1986; Marticorena and Bergametti, 1996 and Callot et al. 2000). The main source areas of mineral dust particles have the characteristic of accumulating large quantities of very fine grain size crustal material produced by the erosion of arid areas during strong rain periods (Prospero, 1999). During the dry season this fine material can be resuspended.

Once in the atmosphere, the mineral particles can be transported long distances. The air masses originated in Northern Africa are transported mainly in three ways:

1) Crossing the Atlantic Ocean towards North, Centre or South America. This transport is very frequent and intense (Goudie, 2001; Schütz, 1981; D'Almeida, 1986). There are many studies documenting this transport of air masses from North

Africa to the Caribbean Area (Prospero and Nees, 1986 Carlson and Prospero, 1972; Prospero et al., 1999 and 2002).

2) Crossing the Mediterranean towards Southern Europe, sometimes even reaching Centre and Northern Europe. This transport is important due to the proximity of the continents. It is associated to determinate meteorological scenarios (Rodriguez et al. 2001; Escudero et al. 2005) and even if it is more episodic that the transport to the Atlantic it produces important increases on the levels of PM. The transport of mineral dust from Northern Africa to Europe and its impact on levels of particulate matter in the atmosphere has been widely studied by Bücher and Lucas, 1984; Avila and Rodà, 1989; Wheeler, 1986; Reiff et al. 1986; Littman, 1991; Loÿe-Pilot et al., 1986; Bergametti et al., 1989; Dayan et al., 1991; Chester et al., 1996; Molinaroli et al., 1993; Ávila et al., 1997, 1998, 1999; Díaz y Miranda, 1997; Guerzoni et al., 1997; Rodríguez et al., 2001, 2002a and b; Viana et al., 2002; Querol et al., 1998, 2002).
3) Towards the Eastern Mediterranean and Middle East. The transport of particulate matter over the Eastern Mediterranean occurs mainly in spring (Goudie, 2001; Ganor and Foner, 1996). The Eastern Mediterranean is also affected by the transport of mineral dust from the Arabian desert (Dayan, 1991; Kubilay et al. 2000).

The transport of mineral dust from Northern Africa to the Iberian Peninsula has been widely studied and documented. Rodriguez et al. (2001), Querol et al., (2002) and Escudero et al. (2004) describe the transport of air masses from Northern Africa to the Iberian Peninsula to be produced in four main meteorological scenarios:

1) North Africa high located at surface level (NAH-S). This scenario favours the transport of air masses at low levels from Western Sahara, Mauritania and the Sahel. This situation occurs mainly in winter.
2) Atlantic depression (AD). This scenario favours also the transport of air masses at low levels from Western Sahara, Mauritania and the Sahel. It occurs also in winter.
3) North African depression (NAD). This scenario may cause airflow from Algeria, Tunisia, Libya and Chad and the air masses are transported through the Mediterranean and are associated with precipitations.
4) North African high located at upper levels (NAH-A). This scenario favours the transport from the Western Sahara, Mauritania and Algeria but at high altitudes and is produced in May and the summer months.

Mineral dust composition depends on the geology of the emission area. The major components are Al, Ca, Si, Fe, Ti, K and Mg. Other important trace elements are Co, Rb, Ba and Sr (Chester et al., 1996; Bonelli et al., 1996). SiO_2 and Al_2O_3 are found (Goudie and Middleton, 2001) due to the presence of quartz and clay minerals. The concentrations of Fe_2O_3, MgO, CaO and K_2O are also relevant due to the occurrence of other alumino-silicates, oxides and carbonates. Northern Africa is also an important source of P. The main mineral composition of mineral dust found in PM is quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), clay minerals, mainly kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($K(Al,Mg)_3SiAl_{10}(OH)$), smectite ($(Na,Ca)Al_4(Si,Al)_8O_{20}(OH)_4 \cdot 2H_2O$ and palygorskite $(Mg,Al)_5(OH)_2[(Si,Al)_4O_{10}]_2 \cdot 8H_2O$, and feldspars like the microcline/orthoclase ($KAlSi_3O_8$) or the albite/anorthite $(Na,Ca)(AlSi)_4O_8$). In minor quantities calcium sulphate ($CaSO_4 \cdot 2H_2O$) and iron oxides (Fe_2O_3) can be found (Glaccum y Prospero, 1980; Ávila et al., 1997; Querol et al., 2002).

The grain size of particles transported varies with the source area and the distance to the emitting source. In episodes of mineral dust transport to America through the Atlantic the main grain size found are accumulation mode particles (0.1-1 μm, Prospero and Carlson, 1981) due to the segregation of the material during transport. The North African dust episodes registered in the Mediterranean during the summer or the Canary Islands during the winter affect mainly the coarse grain size (1-25 μm, Rodríguez et al., 2001).

3. PREVIOUS STUDIES

The present study is continuation of previous studies carried out by the Environmental Geochemistry research group at the Institute of Earth Sciences 'Jaume Almera'. Some previous studies will be outlined.

- TSP and PM_{10} levels and speciation started to be measured already from 1995 at the Teruel coal-fired power station (Querol et al., 1996, 1998a and 1998b) and the relevance of the African dust contribution to the PM levels measured in Spain was highlighted.
- Between 1999 and 2000 PM_{10}, $PM_{2.5}$ and PM_1 levels and PM_{10} and $PM_{2.5}$ speciation were measured at L'Hospitalet-Gornal (Barcelona) and Monagrega (Teruel) monitoring sites (Rodriguez, 2002a).
- In 2001, PM_{10}, $PM_{2.5}$ and PM_1 levels and PM_{10} and $PM_{2.5}$ speciation were measured at the Sagrera monitoring site in Barcelona (Viana, 2003).
- In 2002, PM_{10} $PM_{2.5}$ and PM_1 levels and TSP and $PM_{2.5}$ speciation started to be monitored at the Montseny regional background site. TSP speciation was measured instead of PM_{10} because of the simultaneous studies of dry and wet deposition carried out at the same place (Castillo, 2006). Simultaneously, PM_{10}, $PM_{2.5}$ and PM_1 levels and TSP and $PM_{2.5}$ speciation started to be measured in two monitoring sites in Tenerife, an urban background site at Santa Cruz de Tenerife and a free troposphere remote monitoring site in Izaña.
- From March 2003 to June 2005 PM_{10}, $PM_{2.5}$ and PM_1 levels, PM_{10} and $PM_{2.5}$ speciation and particle number concentration started to be monitored at the urban background site IJA-CSIC in Barcelona. During the same period PM_{10}, $PM_{2.5}$ and PM_1 levels and PM_{10} and $PM_{2.5}$ speciation were monitored at the Montseny regional background site (Pey, PhD Thesis in progress).
- From July 2005 (this work) the monitoring of PM_{10}, $PM_{2.5}$ and PM_1 levels, PM_{10} and $PM_{2.5}$ speciation and particle number concentration has continued to be measured at IJA-CSIC in Barcelona. Moreover PM_1 speciation has started to be measured. At Montseny, the PM_{10}, $PM_{2.5}$ and PM_1 levels and the PM_{10} and $PM_{2.5}$ speciation monitoring has also continued.

To continue the characterization of PM at Barcelona and Montseny it is necessary to complete the studies already carried out by:

- The study of PM_1 speciation, as it has not been studied yet in this area and PM_1 studies are scarce in Southern Europe.
- The continuation of the particle number concentration monitoring to have a longer temporal series.
- The integration of all the years of PM monitoring to study temporal tendencies in PM levels, speciation, particle number and African dust outbreaks. The large number of data and the extension of the temporal series obtained will allow a representative study on the variability of PM levels and composition.

In the present work I make use of the following data to study the time series of PM levels and speciation and particle number concentration monitored at Barcelona and the PM levels and speciation monitored at Montseny:

- PM levels and speciation monitored between 1999 and 2000 at L'Hospitalet-Gornal urban monitoring site in Barcelona.
- PM levels and speciation monitored in 2001 at the Sagrera urban site in Barcelona.
- PM levels and speciation and particle number concentration monitored at the Barcelona-CSIC urban site from 2003 to 2007.
- PM levels and speciation monitored at the Montseny regional background site from 2002 to 2007.

4. OBJECTIVES

The main objective of this study is the interpretation of the variability of the concentrations (mass and number) of PM_{10}, $PM_{2.5}$ and PM_1 and their chemical composition at an urban and a regional background in North-Eastern Iberian Peninsula and the comparison between both backgrounds.

The specific objectives of this work are:

- The integration of all the data previously obtained at Montseny and Barcelona to study temporal tendencies on PM levels, speciation, particle number concentration and African dust outbreaks.

- The study of the partitioning of the different components of particulate matter between $PM_{2.5-10}$ (2.5 to 10μm), $PM_{1-2.5}$ (1 to 2.5 μm) and PM_1 (<1μm) fractions at an urban site (Barcelona) and between $PM_{2.5-10}$ and $PM_{2.5}$ at a regional site (Montseny) to study the size distribution of the different PM components and to investigate their possible origin.

- The study of the PM_1 levels and composition at an urban background site (Barcelona) and the comparison with the PM_{10} and $PM_{2.5}$ levels and composition simultaneously monitored. PM_1 measurements are nowadays very scarce in Europe. The monitoring of this parameter is important because finer particles are related to stronger health effects than the coarser ones. The study of the composition is necessary to evaluate the main sources that contribute to PM_1 and to compare them with $PM_{2.5}$ and PM_{10} sources. The evaluation of the possibility of using PM_1 as an air quality monitoring parameter is also key point of this study. One reason is that PM_1 can be more directly related to health effects than the coarser particles. Furthermore, the sources contributing to finer particles are more related to anthropogenic emissions than to natural emissions that affect in a higher proportion the coarser fraction.

- The study of the mineral dust load simultaneously monitored at an urban (Barcelona) and a regional background site (Montseny) in the same area can help to quantify the anthropogenic and the natural contribution to the mineral dust load at the urban site and to assess the contribution of African dust, regional soil

resuspension and anthropogenic mineral dust (from road traffic, demolition and construction activities, etc.).

- The interpretation of the particle number concentration at an urban background site (Barcelona) and its comparison with the PM levels simultaneously registered at the same site to study the temporal trends and the seasonal evolution of the levels and the possible relationship of the particle number with the PM levels to assess the possible sources to ultrafine particles. The possibility of monitoring particle number concentration together with PM is also a topic to study because the ultrafine particles have the most important effects on health and an important impact on the earth's radiation balance.

To reach the objectives proposed in this project the following tasks were carried out:

- The interpretation of the variability of PM_{10}, $PM_{2.5}$ and PM_1 levels and speciation at a regional background monitoring site (Montseny) and an urban background monitoring site (Barcelona) in North-Eastern Spain. The monitoring sites were already working from 2002 (Montseny) and from 2003 (Barcelona).
- The continuous monitoring of PM_{10} and $PM_{2.5}$ levels to identify the causes that difficult the compliance with the limit levels established by the Air Quality European Union Directive 1999/30/EC.
- The continuous evaluation of the influence of African dust outbreaks on PM levels and composition at the urban and the regional background sites Barcelona and Montseny.
- The study of the speciation of PM_{10}, $PM_{2.5}$ and PM_1 at Barcelona.
- The study of the speciation of PM_{10} and $PM_{2.5}$ at Montseny.
- The evaluation of particle number concentrations at the urban background site in Barcelona.

5. METHODOLOGY

5.1. Study area

5.1.1. Atmospheric dynamics and transport of pollutants to the study area

The Iberian Peninsula is very influenced by the Azores high pressure system and balanced between two synoptic systems (Millan et al., 1997; Perez et al., 2004; Sicard et al., 2006). In the winter the Azores anticyclone is situated at lower latitudes on the Atlantic Ocean and allows lows and cold fronts to reach the Iberian Peninsula, favouring air mass renovation. In the summer the Azores anticyclone, centred on the Atlantic, intensifies and produces weak pressure gradient conditions all over the region. During this period of the year regional and local factors determine the atmospheric dynamics in the Western Mediterranean. The absence of a big scale forcing and the development of meso-scalar phenomena related with the daily temperature cycle (sea-earth breezes, valley and mountain winds) produce regional pollutant recirculations over the eastern coast of the Iberian Peninsula (Millán et al. 1997 and Rodriguez et al., 2002).

Barcelona is located on the North-western coast of the Iberian Peninsula on the Western Mediterranean (Figure 5.1). The mountain ranges surrounding the area act as a climatic barrier, protecting the area from the continental climatic conditions and influencing the winds arriving in the area. The Pyrenees Range, the Catalan Coastal Ranges and the valleys crossing the coastal ranges (the Ebro, Llobregat and Besòs Valleys) are the main geographical systems of the study area (Figure 5.2). The typical winds in the region are the Tramontana (northern winds affecting the north-eastern peninsula) and the Cierzo (north-western winds canalized by the Ebro valley). The Montseny monitoring site is situated on the Catalan pre-Coastal Range.

These mountain ranges have an orientation northeast-southwest and the heating of the slopes orientated to the east and southeast by the sun during the morning hours activates the sea-land breezes (Baldasano et al., 1994; Millan et al., 1997). Air masses are injected to different heights depending on the breeze intensity. At a certain altitude the atmospheric circulation transports these air masses to the Mediterranean, where there is a subsidence area. In this way an air mass recirculation system is generated producing the aging of the pollutants carried by these air masses. The predominating air mass transport is from the sea to the land (valley and mountain breezes) during the

day and the opposite (through the valleys) during the night. The air masses returning to the sea carry the pollutants accumulated during the day.

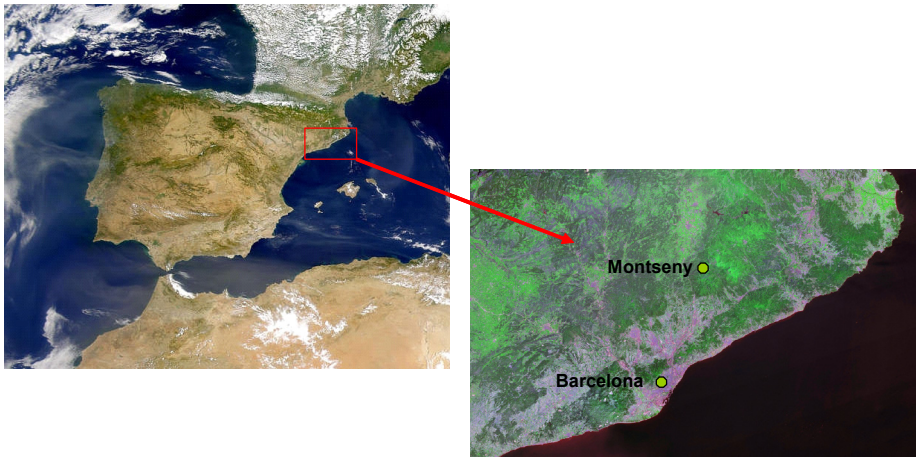

Figure 5.1. Location of the study area.

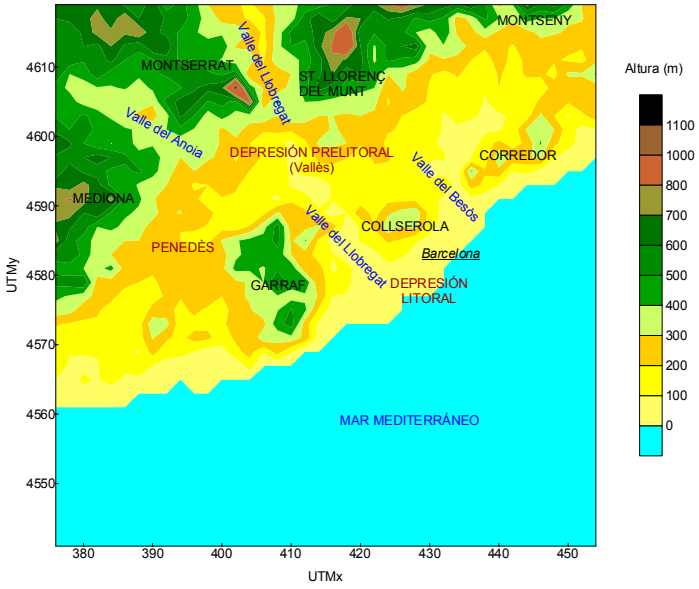

Figure 5.2. Orography of the study area.

From the analysis of atmospheric retro-trajectories, Jorba et al. (2004) described the synoptic transport patterns in the Barcelona area (Figure 5.3). The results show three groups of westerly flows (fast, moderate and slow) being 48% of the analyzed situations at 5500m, 38% at 3000 m and 23% at 1500 m.

In winter, the worst situation for air quality is the high pressure system induced by the presence of the continental anticyclone. In this situation, the precipitations have a low influence, the thermal amplitude is high and the wind speed is lower than the average.

A thermal inversion of a few hundred of metres is formed over the ground and it prevents air mass ascending movements, with a significant increase of pollutants at surface levels, especially primary gaseous pollutants and particulate matter. These situations are characterized by their temporal persistency, sometimes longer than one week.

In summer, there is a high occurrence of regional air mass re-circulation situations, being the 45% of the total situations (Figure 5.3). They are characterized by the stagnation of air masses during periods of several days, with the formation of diurnal sea-earth and nocturnal earth-sea breezes and mountain winds. As a typical characteristic of the region when compared with more septentrional regions there is an important decoupling between the low and middle troposphere, especially in summer, with zonal fluxes in middle and high layers of the troposphere and stagnation in the lower levels.

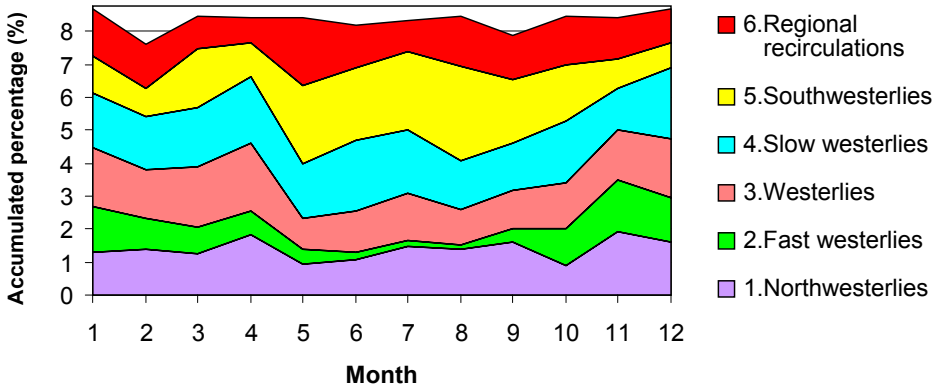

Figure 5.3. Cluster analysis of retro-trajectories ending in Barcelona (Jorba et al., 2004).

PM levels and composition are conditioned by the influence of anthropogenic emissions, the local, regional and synoptic meteorological conditions and the dispersion of pollutants inside the boundary layer. Winter pollution episodes are mainly dominated by stable anticyclonic conditions, which favour air mass stagnation and thus result in high levels of PM. The summer months are characterised by the absence of large-scale forcing and the predominance of mesoscale circulations (Figure 5.4): the formation of a thermal low at a peninsular level forcing the convergence of surface winds from the coastal areas towards the central plateau with strong levels of subsidence over the Western Mediterranean Basin and sea-land breeze dynamics

which result in the recirculation and accumulation of pollutants over the eastern Iberian coast. Breeze circulations and transitions (diurnal sea breeze and weak nocturnal earth breeze) are reflected in PM concentrations. Levels and time variations of PM are determined by traffic emissions together with the sea breeze system and the structure of the boundary layer.

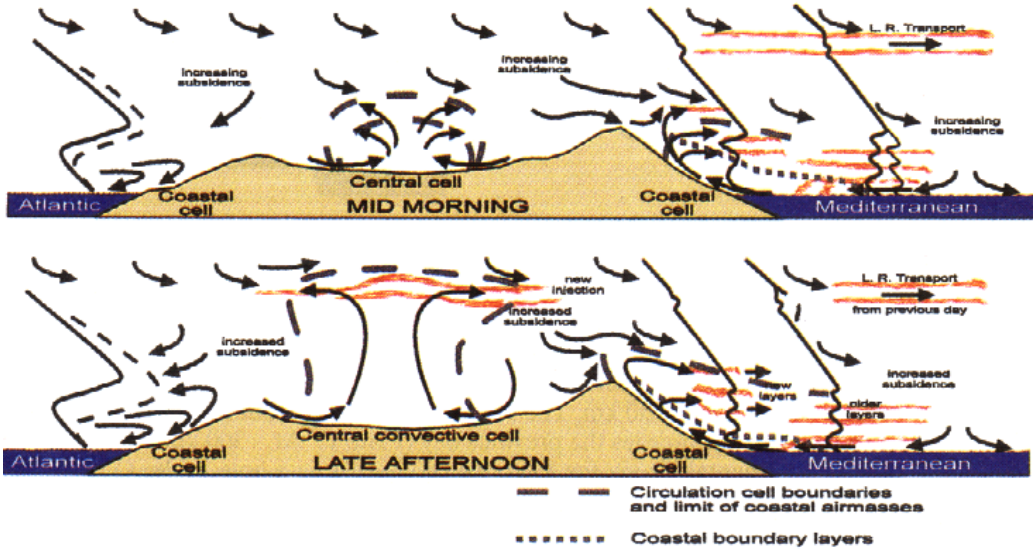

Figure 5.4. Typical summer atmospheric circulation at mid morning and late afternoon over the Iberian Peninsula (Millán et al., 1997)

The analysis of air mass circulation at a local scale was performed by analyzing wind velocity directions and data from meteorological stations near the study monitoring sites (Figure 5.5). Based on the data available at the meteorological station of Tagamanent from the Servei Meteorologic de Catalunya (http://www.meteocat.com), two main wind directions were identified at Montseny: south-south-west, when the mountain breezes develop, and north-north-west corresponding to the intense northern and north-western advections and also to the drainage flow across the valley during the night. Both wind directions are conditioned by the orography of the valley where is situated the meteorological station Tagamanent. During the winter the main wind direction is north and north-west and during the rest of the year it is the south direction, reaching the highest wind velocity during the day. In Montseny, during the winter, the monitoring site is placed for long periods out of the boundary layer and the levels of pollutants are low. The pollutants from the area accumulate in the Vallès valley for periods of several days during these thermal inversion periods. When mountain breezes develop they carry the pollutants to the monitoring site and peaks of pollution are recorded. During the summer the site is affected by the mountain and sea breezes and is located inside of the boundary layer.

In Barcelona the main wind direction is south-west (Data from the Department of meteorology and climatology of the Facultat de Química i Física of the Universitat de Barcelona). The air mass circulation at Barcelona is less conditioned by the orography of the area. The south-western wind direction corresponds to western advections and to the day sea-land breezes. During the night the drainage flows take the north-east direction.

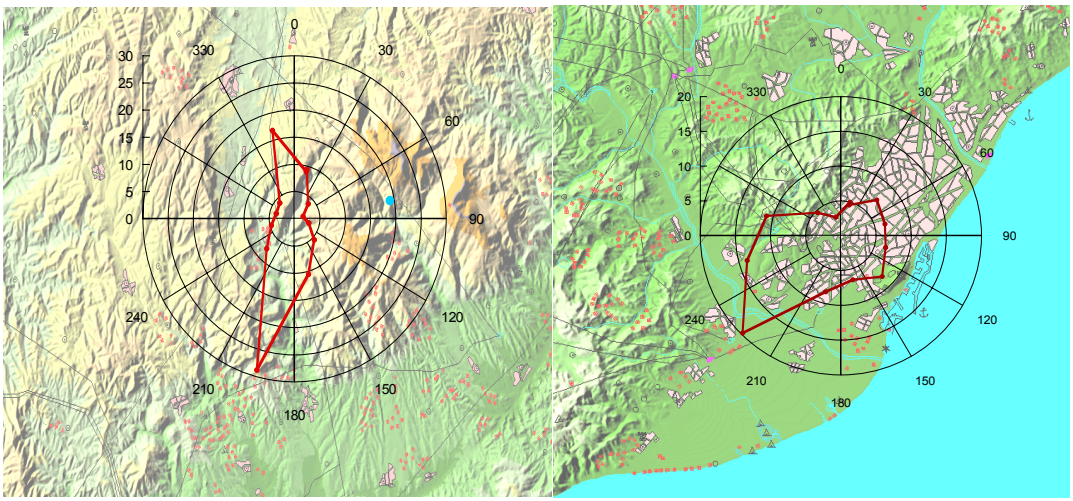

Figure 5.5. Relative frequencies of main wind directions at Tagamanent meteorological station (left, Servei Meteorològic de Catalunya) and Barcelona (right, Departament de Meteorología i Climatología of the Facultat de Química i Física of the Universitat de Barcelona).

The main source of atmospheric particulate matter in Barcelona is traffic with a high impact on the levels of carbonaceous compounds, nitrate and mineral matter. Other disperse sources (small industries, house heatings, etc.) contribute to the increase the levels of sulphate, nitrate and carbonaceous compounds. Construction activities have an important impact on the levels of coarse mineral compounds.

Atmospheric particulate matter at Montseny is mainly fine (Castillo, 2006). In addition to the natural origin PM, the main sources are urban, industrial, and agricultural and farming emissions at a regional scale and it is mainly composed of ammonia sulphates and nitrates and carbonaceous compounds that can be associated to anthropogenic or biogenic emissions. The main source to the mineral dust is the regional and local soil resuspension and in a minor extent the African dust outbreak contribution.

5.1.2. Barcelona monitoring site

The PM monitoring site in Barcelona is an urban background station under the influence of the emissions of road traffic from one of the largest avenues at the western edge of the city (Figure 5.4). The monitoring station is located on the roof of the Institute of Earth Sciences "Jaume Almera" (41º23'N and 2º7'E at 68 m.a.s.l.). The building has two storeys and is found within the University campus at approximately 150 m distance from the Diagonal Avenue. The mean annual temperature is 17.4ºC, the mean relative humidity 77% and the mean precipitation 487 mm (Ayuntamiento de Barcelona).

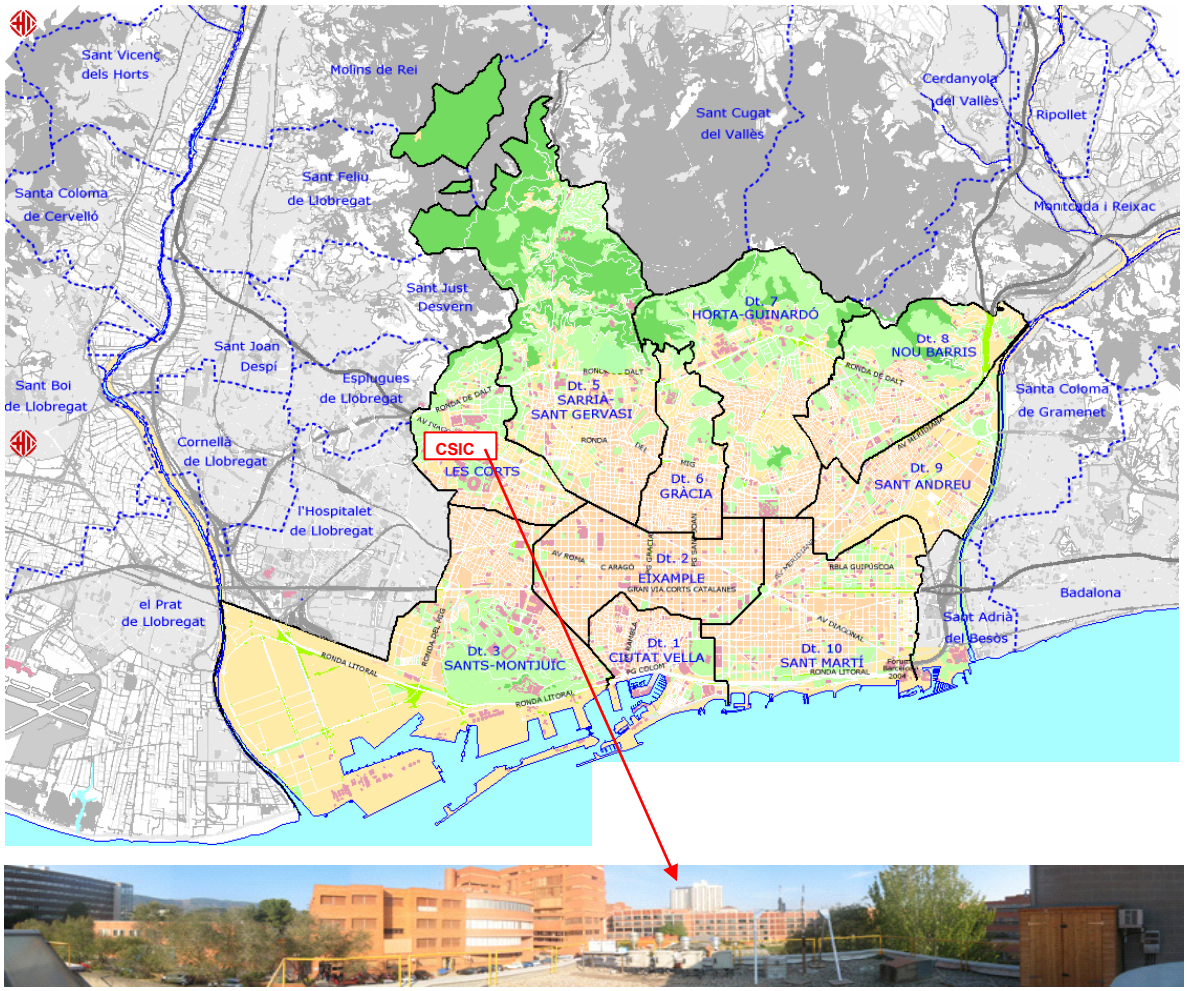

Figure 5.4. IJA-CSIC PM monitoring site at Barcelona.

The Barcelona-CSIC site is operating since March 2003. It is equipped with laser spectrometer dust monitors (Grimm Labortechnik GmbH &Co. KG) for the continuous measurement of PM_{10}, $PM_{2.5}$ and PM_1 levels. Twenty four hours samples of PM_{10}, $PM_{2.5}$ and PM_1 were simultaneously collected on quartz micro-fibre filters (Schleicher and Schuell, QF20) by means of high-volume samplers equipped with PM_{10}, $PM_{2.5}$ and

PM_1 (the latter since October 2005) inlets (DIGITEL, 30m^3/h). Sampling was carried out at a rate of 2 24h samples of each PM fraction per week.

Aerosol number concentration has been monitored from 2003 to 2005 with a butanol-based condensation particle counter (TSI CPC 3022A) and from 2005 with a water-based condensation particle counter (TSI WCPC 3785).

Data relative to levels, chemical composition and particle number in Barcelona from 2003 to June 2005 are obtained from the PhD Thesis of Jorge Pey, currently in progress and partially published in Querol et al. (2004a and 2007). Data from other sites in Barcelona from 1999 to 2002 are used to help the interpretation of results. These sites were L'Hospitalet-Gornal (1999-2000, Rodriguez, 2002), La Sagrera (2001, Viana, 2003) and Zona Universitaria (2002, Barcelona Air quality Monitoring Network).

5.1.3. Montseny monitoring site

There are currently several networks for measuring atmospheric aerosols in Spain. They are generally located in urban areas and they are designed to determine levels of the different granulometric fractions of PM with the end of evaluating the agreement with the existent directives and provide data for epidemiologic studies. Nevertheless, it is necessary to have other networks located in background areas without direct local emissions. This strategy allows the estimation of the increment in pollution attributed to urban emissions and helps to understand the transport processes of aerosols at a regional and intercontinental scale to design appropriate strategies to reduce pollution levels.

The Montseny monitoring site is a regional background site for the measurement of atmospheric aerosols (Figure 5.5.). It is located in *La Castanya* an experimental ground owned by the *Generalitat de Catalunya* in the Montseny Natural Park (40 km to the North-East of Barcelona, 25 km from the Mediterranean coast, 41º46'N and 2º21'E, 720 m.a.s.l.).The Montseny is part of the pre-coastal Catalan mountain range. The clima of this area is characterized by a mean annual temperature of 14ºC and a precipitation ranging between 600 and 1660 mm. It has been operating from February 2002 and the results obtained provide important information about tropospheric aerosols in the Mediterranean area. This site is integrated in the Network of Control and Surveillance of Air Quality of the *Direcció General de Qualitat Ambiental* of *the Conselleria de Medi Ambient* of the *Generalitat de Catalunya* and in the European

supersite network EUSAAR (EUSAAR, *European Super-sites for Atmospheric Aerosol Research*).

The Montseny site is equipped for the continuous real time measurement of PM_{10}, $PM_{2.5}$ and PM_1. From 2002 to the end of 2003, TSP and $PM_{2.5}$ were sampled periodically for chemical characterization and from January 2004 PM_{10} y $PM_{2.5}$ were sampled.

Data relative to levels and composition of Montseny from 2002 to July 2005 are obtained from the PhD Thesis of Sonia Castillo (Castillo, 2006) and Jorge Pey, currently in progress and partially published in Querol et al. (2004a and 2007).

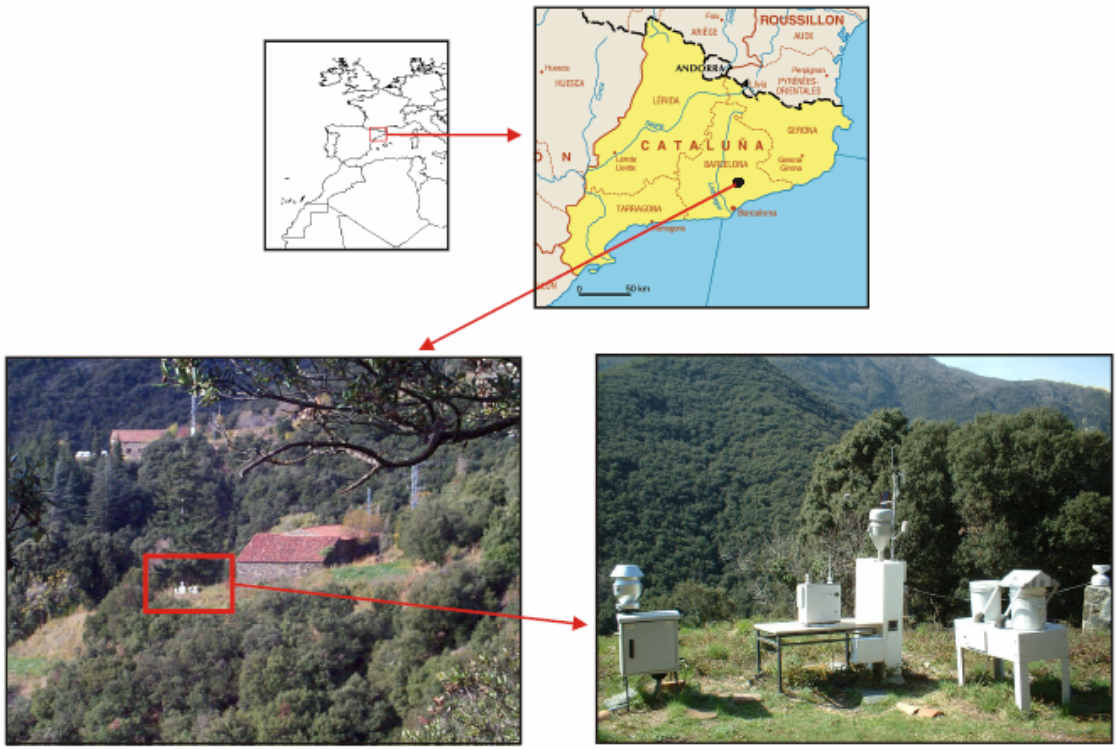

Figure 5.5. Montseny monitoring site.

5.2. PM measurement: instruments and methods

5.2.1. Instruments

Real time measurements of PM concentration levels

The levels of PM_{10}, $PM_{2.5}$ and PM_1 were measured continuously in an hourly basis by means of laser-spectrometer dust monitors (Grimm Labortechnik GmbH &Co. KG. 1107 and 1108 models, Figure 5.6). These measure particle concentration levels between 0.3 and 15µm. The operation principle is based in the measure of particle number. Particles pass through a laser beam and generate signals at different wavelengths as a function of their diameter. These signals are registered by a detector and the number of counts registered is converted to mass by an algorithm and expressed in $\mu g/m^3$. The data obtained in this study is corrected using the gravimetric PM_{10} and $PM_{2.5}$ (and PM_1 in Barcelona from October 2005) data obtained simultaneously with high volume samplers.

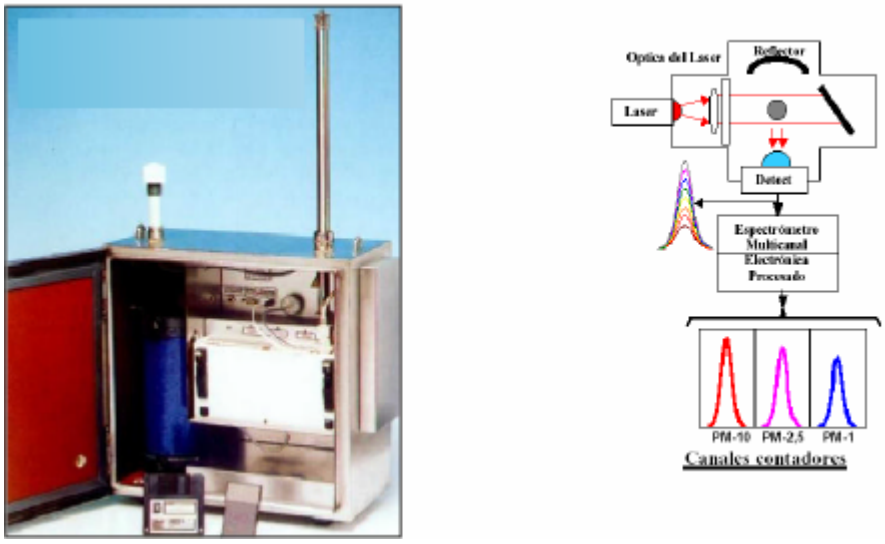

Figure 5.6. GRIMM 1107 dust monitor and flow diagram (SIR S.A).

PM sampling

Twenty four hour samples of PM_{10}, $PM_{2.5}$ and PM_1 were simultaneously collected in Barcelona on quartz micro-fibre filters (Schleicher and Schuell, QF20) by means of high-volume samplers (MCV PM1025-CAV) equipped with PM_{10}, $PM_{2.5}$ and PM_1 inlets (DIGITEL and MCV) at $30m^3/h$. Sampling was carried out at a rate of 2 samples of each PM fraction per week (Figure 5.7).

An automatic sequential high volume sampler (DIGITEL DH80) working at $30m^3/h$ was used in Montseny for the sampling of PM10 fractions. 3 samples per week were

collected. PM2.5 was sampled by means of a MCV high-volume sampler at a rate of 1 filter per week (Figure 5.7).

In these instruments the air enters through the inlet, vacuumed by the sampler and goes through tubes of a diameter depending of the fraction to sample, where it increases its speed. Then there is an impact plate impregnated with Vaseline. The particles bigger than the designed cut size are collected there and the smaller ones will pass and be collected on the filter.

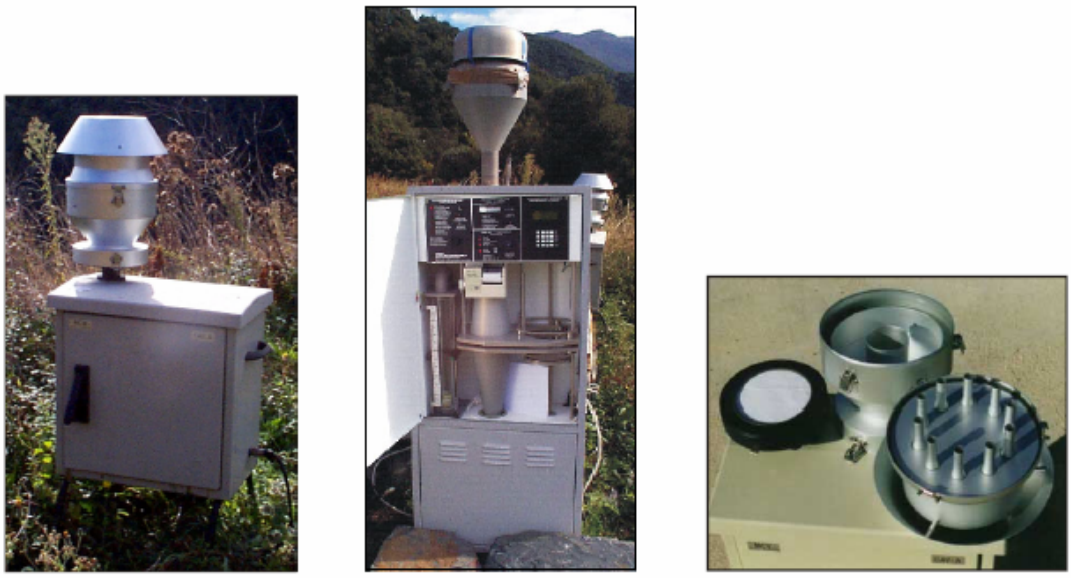

Figure 5.7. MCV CAV-HA High volume sampler (left). DIGITEL DH80 high volume sampler (centre). Detail of the MCV CAV-HA PM10 inlet (right)

Measurement of particle number concentration

The levels of sub-micron particle number concentration in the range 3nm-3μm were monitored from June 2005 from June 2007 at the Barcelona urban background site by means of a water-based condensation particle counter (TSI WCPC 3785, Figure 5.8). Before this study, particle concentration in the range 13-800 nm was monitored during November 2003 to December 2004 by means of a butanol-based condensation particle counter (TSI CPC 3022A). We started to use a water-based CPC instead of a butanol-based CPC at Barcelona because we had problems with flooding of the butanol because of the high relative humidity at the monitoring site.

The WCPC is designed to measure the concentration of airborne ultrafine particles and counts the number of particles to provide a value displayed as particle number by cubic centimetre of sampled air. The WCPC uses a laser and an optical detector to detect

particles. Ultrafine particles are not easy to detect because their diameters are equal or smaller than light wavelength. For these reason, a saturation system is used. The aerosol enters the sample inlet and immediately enters a region supersaturated with water vapour. Then it passes through the growth section were the walls are heated to produce an elevated vapour pressure. Water condenses on particles as it passes through the growth tube and the enlarged particles can be then detected by the optical detector. The minimum detectable particle diameter is 3 nm (for wettable aerosols) and the maximum particle diameter that is detected is 3 microns. Figure 5.8 shows the scheme of a WCPC.

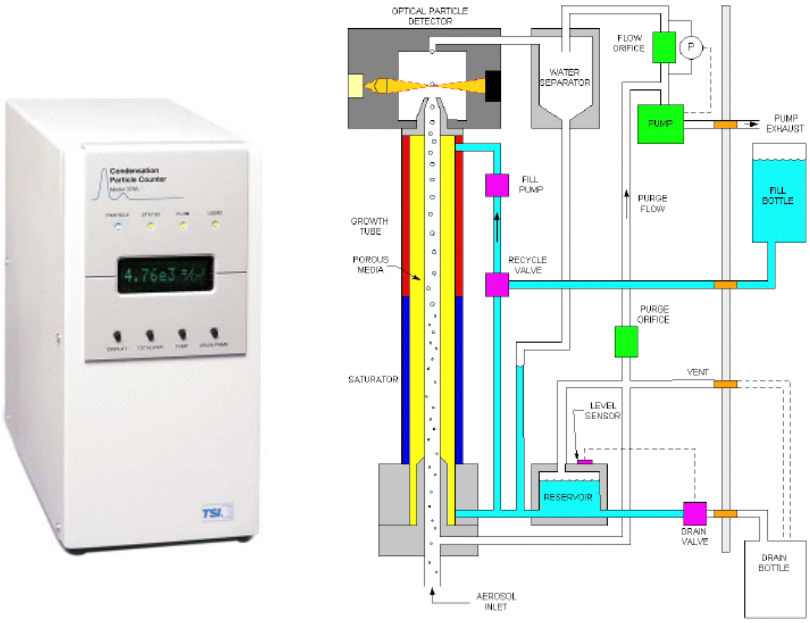

Figure 5.8. Water-based condensation particle counter and flow diagram (TSI WCPC 3785 operation and service manual).

5.2.2. Chemical characterization of particulate matter

Filter conditioning

The sampling was carried out by means of high volume samplers using 150 mm diameter Quartz micre fibre filters (Schleicher and Schuell, QF20). The filters were pre-heated at 200ºC during four hours to eliminate the volatile compounds. Then, the filters were conditioned under controlled temperature and humidity during 24 hours. After that, the filters were weighted during three consecutive days to be certain of the blank filter weight. Then, they were preserved individually in aluminium foil until they were used for sampling. Every fifteen filters three filters were separated to be used as blanks for chemical analysis.

After sampling, the filters were conditioned at controlled temperature and humidity again and stabilized during 24 hours. They were weighted during at least two consecutive days to get a definitive weight. From the mass and the volume of air of sampling it was possible to determine the mean concentration during the sampling period.

Analytical procedure

Once the gravimetric determination is performed, the filter can be analyzed.

The filters were cut. ½ of each filter was acid digested (2.5 ml HNO_3 and 5 ml HF) into a PFA pot at 90ºC during at least 8 hours. After cooling 2.5 ml $HClO_4$ were added and then acids were completely evaporated on a heating plate at 200ºC. The dry residue was dissolved with 2.5 ml HNO_3 adding bi-distilled water (MilliQ) up to 50 ml and obtaining a solution of 5% HNO_3. This solution was analyzed for the determination of major and trace elements by ICP-AES and ICP-MS.

In every analysis blank filters were analyzed by the same procedure. The blank filter analysis is useful to control the levels of the elements in the blank filters and to subtract the concentrations to those obtained for the filters sampled.

5 mg of a certified reference material (NBS1633b, fly ash) was also analyzed loaded on ½ blank filter. The reference material analysis assures the quality of the results permitting the identification of possible analytical or calibration errors.

Another ¼ of each filter was water leached for the determination of soluble ion concentrations by ion chromatography (sulphate, nitrate and chloride) and FIA colorimetry (ammonium). The filter portion is cut in pieces and introduced into a PVC pot with 30 ml of bi-distilled water. It was placed in an ultrasound bath during ten minutes and then heated at 60ºC during 6 hours. After this, the liquid is filtrated and then it is ready to be analyzed.

The remaining ¼ of each filter was used for the elemental analysis of total carbon.

Analytical techniques

ICP-AES. Inductively coupled plasma Atomic Emission Spectrometry for the determination of major elements (Al, Fe, K, Ca, Na, Mg, S, P, Ba, Cr, Cu, Mn, Ni, Sr, Pb, Ti, V, Zn). These analyses were carried out at the Laboratory of ICP MS/AES in the Institute of Earth Sciences 'Jaume Almera', CSIC.

ICP-MS. Inductively coupled plasma Mass Spectrometry for the determination of trace elements (Li, Be, B, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu,

Hf, Ta, W, Tl, Pb, Bi, Th and U). These analyses were carried out at the Laboratory of ICP MS/AES in the Institute of Earth Sciences 'Jaume Almera', CSIC.

IC. Ion chromatography for the determination of water soluble ions (Cl^-, NO_3^- and SO_4^{2-}). These analyses were performed partly at the Institute of Earth Sciences 'Jaume Almera', CSIC and partly at the University of Granada.

Ammonia selective electrode for the determination of NH_4^+. This analysis were carried out at the Institute of Earth Sciences 'Jaume Almera', CSIC.

Carbon elemental analyzer for the determination of the total carbon contents of the samples. These analyses were carried out at the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT).

With these analytical techniques it was possible to determine up to 63 components. Some of these have been indirectly determined using empirically obtained factors as SiO_2 ($3*Al_2O_3=SiO_2$) and CO_3^{2-} ($1{,}5*Ca=CO_3^{2-}$). The non-mineral carbonaceous compounds are expressed as the sum of organic matter and elemental carbon (OM+EC). The concentration of OM+EC is calculated from the total carbon content. First, the mineral carbon from carbonates is subtracted to the total carbon ($OC+EC=Ctotal-0.2*CO_3^{2-}$). The ratio between EC and total carbon was estimated from the OC-EC analysis performed by J.Pey (PhD Thesis in progress) to be 0.15 for Montseny and 0.25 for Barcelona. To calculate the organic matter component (OM) the OC is multiplied by a factor with the intention of adding the heteroatoms (H, N, O) not analyzed with this method. This factor was estimated by various authors to be between 1.2 and 2.1, higher for remote sites and lower for urban sites (Lynn M. Russell, 2003, Putaud et al., 2000, Turpin et al. 2001). We applied a factor of 1.4 for Barcelona and of 1.6 for Montseny. With these ratios and factors the next calculations were made:

Barcelona: $OM+EC= 0.25*Ctotal+0.75*Ctotal*1.4$

Montseny: $OM+EC= 0.15*Ctotal+0.85*Ctotal*1.6$

From 75 to 85% of the PM_{10}, $PM_{2.5}$ and PM_1 mass was accounted from the addition of the above determinations. The remaining undetermined mass is attributed to the formation and adsorbed water that was not removed during the sample conditioning.

The chemical components of the PM were grouped as:

(a) crustal or mineral (sum of elements typically found in rock-forming minerals, including Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P)

(b) marine component (sum of Cl^- and Na^+)

(c) carbonaceous compounds (organic matter and elemental carbon, OM+EC)
(d) secondary inorganic species, SIA (sum of non-marine SO_4^{2-}, NO_3^- and NH_4^+ concentrations).

Relative analytical errors were estimated using the NIST-1633b (fly ash) reference material. These reached values <10% for most elements, with the exception of P and K (<15%).

5.3. Interpretation of the origin of air masses: meteorological and aerosol models and satellite images

Additional tools were used for the interpretation of PM levels and for the subsequent analysis of the chemical characterization results, like meteorological maps, aerosol models and satellite images. These tools are all freely available on the Internet.

Air mass back-trajectory analysis was performed at 750, 1500 and 250 m.a.s.l. using the Hysplit model of the NASA (Draxler and Rolph (2003) http://www.arl.noaa.gov/ready/open/hysplit4.htm). From the back-trajectories (calculated for 120 hours) it is possible to establish approximately the origin of air masses that reach a determined area, especially when transport comes from a long distance. For the study area considered, the next origins are distinguished (Figure 5.9): Northern Atlantic (NA), North-western Atlantic (NWA), Western Atlantic (WA), South-Western Atlantic (SWA), North African (NAF), distant Mediterranean (MED), Centre Europe (EU) and Regional (REG). Nevertheless, the information obtained needs to be complemented with other means.

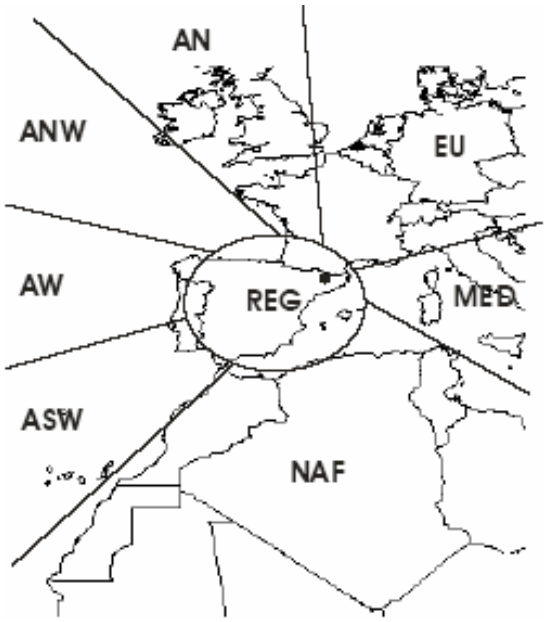

Figure 5.9. Map of air mass origin for the area of the study

NAAPS Aerosol maps from the Marine Meteorology Division of the Naval Research Laboratory (NRL, http://www.nrlmry.navy.mil/aerosol). They provide information on the aerosol optical depth and on the surface concentration of sulphate particles, mineral dust from desert areas and carbonaceous aerosols derived from biomass burning (Figure 5.10).

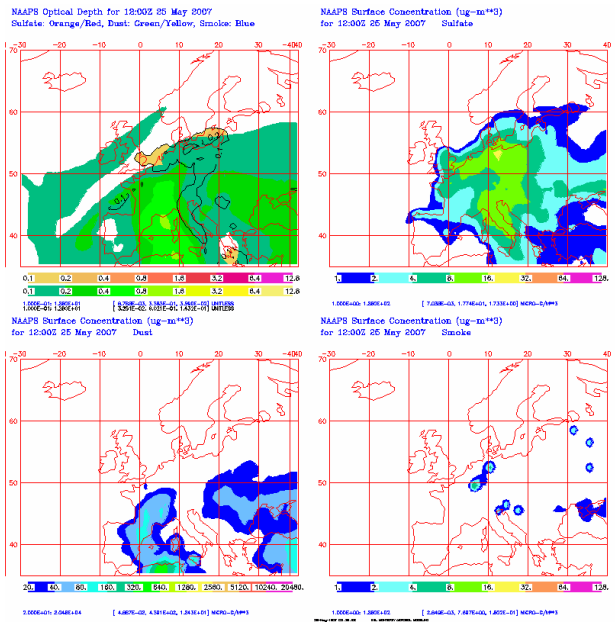

Figure 5.10. NAAPS aerosol maps

SKIRON aerosol maps (http://www.forecast.uoa.gr, Kallos et al., 1997) provide mineral dust prediction maps every 6 hours (Figure 5.11). The maps provide information about total and surface dust load and about dry and wet dust deposition at a surface level.

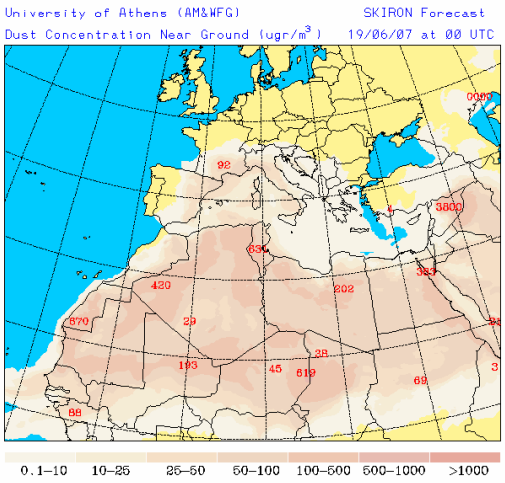

Figure 5.11. SKIRON dust concentration map.

BSC-DREAM maps of dust origin mineral particle concentration (http://www.bsc.es/projects/earthscience/DREAM.html). The maps are composed of a meteorological map with isobars at a surface level and the precipitation prediction and an aerosol map showing areas affected by dust and expected concentrations at a surface level (Figure 5.12). With these maps it is possible to identify the emission source areas of mineral dust.

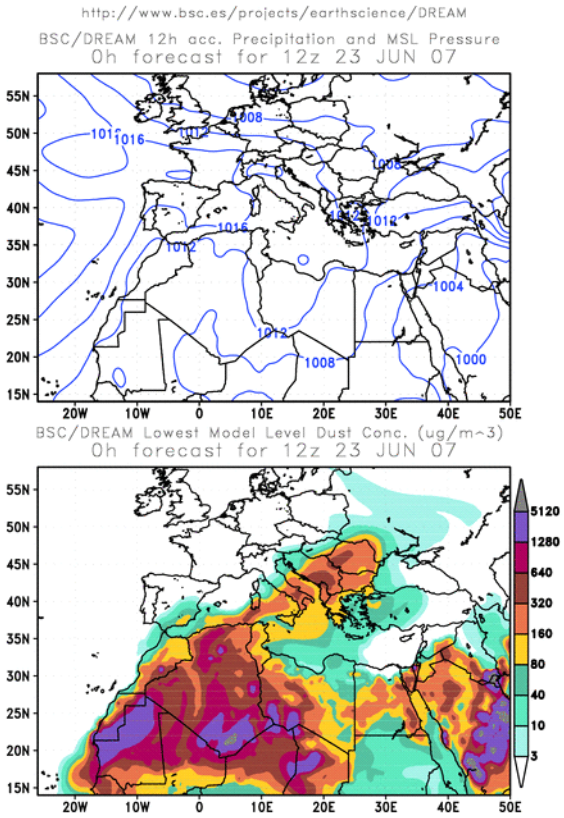

Figure 5.12. BSC-DREAM dust concentration maps

NASA SeaWIFS satellite images (McCLain et al., 1998. SeaWIFS Project Image Archive, http://seawifs.gsfc.nasa.gov/SEA-WIFS.html). These images (Figure 5.13.) are very useful to visualize the dust transport over the sea but they have a few limitations. The transport height of dust and the possible impact on surface cannot be known, over the land it is difficult to distinguish the dust and it can be superposed with clouds. Besides these limitations, this tool is very useful in this kind of studies, permitting the validation of the models.

Figure 5.13. SeaWIFS Satellite image for Northern Africa and the Mediterranean. A dust mass can be observed over the Atlantic.

MODIS Rapid Response System satellite images (Earth and Aqua satellites, http://rapidfire.sdci.gsfc.nasa.gov.html). The images provided by these satellites are very useful to identify the transport of mineral dust from desert areas, even seen over continental areas and to localize forest fires and biomass burning (Figure 5.14.).

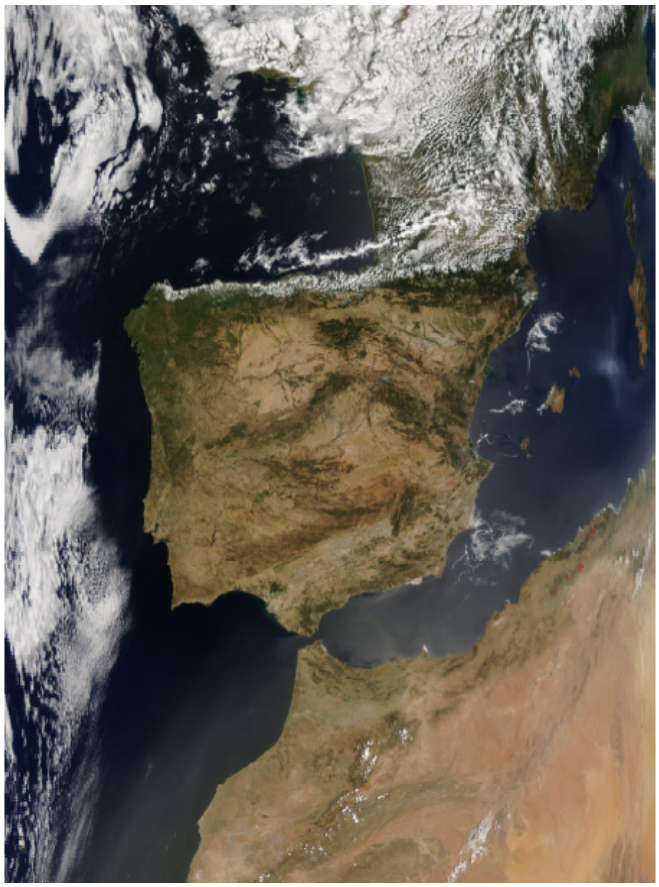

Figure 5.14. MODIS Earth satellite image over the Iberian Peninsula.

6. RESULTS AND DISCUSSION

In this chapter, the PM levels and speciation recorded at the Barcelona urban background and at the Montseny regional background sites are presented, discussed and compared. Special attention is paid on the PM speciation and grain size partitioning between the different PM fractions for the Barcelona and Montseny sites. The contribution of mineral load to the PM levels at the urban background is evaluated by comparing the PM crustal load at Barcelona and Montseny to quantify the contribution of external and local sources to the mineral load at the urban site. Finally the number concentration levels monitored at Barcelona are presented and discussed and then compared with the PM levels.

6.1. PM levels at Barcelona and Montseny

6.1.1. Mean PM levels and inter annual trends

PM levels were registered at Barcelona from 1999 (four different sites) and at Montseny from 2002 by means of laser spectrometer dust monitors GRIMM with levels being corrected with the factors obtained by comparison with the simultaneous gravimetric monitoring with high volume samplers. The mean annual PM_{10}, $PM_{2.5}$ and PM_1 levels registered at Barcelona from 1999 and at Montseny from 2002 are shown in Table 6.1. The daily PM levels recorded at these sites are shown in Figures 6.1 and 6.3. The annual mean PM levels are shown in Figures 6.2 and 6.4.

Table 6.1. PM mean annual levels registered at Barcelona from 1999 to june 2007 and at Montseny from 2002 to june 2007. Barcelona data data were obtained at four different sites: [a]L'Hospitalet-Gornal (Rodriguez, 2002); [b]Sagrera (Viana, 2003); [c]Zona Universitaria (Barcelona Air Quality Monitoring Network); [d]IJA-CSIC (unpublished data from J.Pey PhD Thesis in progress and this work).

PM levels	Barcelona			Montseny		
$\mu g/m^3$	PM_{10}	$PM_{2.5}$	PM_1	PM_{10}	$PM_{2.5}$	PM_1
1999 [a]	42	21	12			
2000 [a]	48	23	14			
2001 [b]	44	26	18			
2002 [c]	29**			20	16	12
2003 [d]	40	25	19	20	15	12
2004 [d]	39	25	21	19	15	13
2005 [d]	39	27	21	14	11	10
2006 [d]	42	29	20 (23)*	14	11	9
2007 [d]	37	23	18 (19)*	12	9	8
Mean	41	25	18	17	13	11

*PM_1 measurements are corrected with gravimetric PM_1 data from October 2006 in Barcelona. If corrected with $PM_{2.5}$ gravimetric data like in the years before, the PM_1 levels increase to the number in parentheses. **PM_{10} measured at Zona Universitaria site in Barcelona is anomalously low. It is not considered for the mean PM levels calculation.

The levels measured by the gravimetry method using high volume samplers are slightly higher (Table 6.2). These differences with the levels measured in continuous were due to the fact that high volume sampling was done only on weekdays, when traffic density and other anthropogenic emissions are higher, whereas the real time measurements also covered weekends. These differences are more marked at Barcelona as it is more influenced by anthropogenic emissions.

Table 6.2. PM mean annual levels registered at Barcelona from 1999 and at Montseny from 2002 by gravimetry. Barcelona data data were obtained at different sites: [a]L'Hospitalet-Gornal (Rodriguez, 2002); [b]Sagrera (Viana, 2003); [c]Zona Universitaria (Barcelona Air Quality Monitoring Network); [d]IJA-CSIC (unpublished data from J.Pey PhD Thesis in progress and this work).

PM levels	Barcelona				Montseny			
µg/m^3	TSP	PM_{10}	$PM_{2.5}$	PM_1	TSP	PM_{10}	$PM_{2.5}$	PM_1
1999-2000 [a]	50		34					
2001 [b]	46		28					
2002 [c]					29		15	
2003 [d]		46	28		26		16	
2004 [d]		49	35			19	19	
2005 [d]		45	31			16	13	
2006 [d]		45	29	18		15	14	
2007 [d]		44	32	19		12	11	
Mean	48	46	31	19	28	16	15	

The high PM levels recorded at Barcelona have an anthropic origin. The main sources contributing to PM in this urban area are road traffic, industrial activities, energy generation, waste treatment plants and port activity. PM levels measured at Barcelona can be considered as relatively high when compared with the average ranges observed at urban and industrial background sites in Spain, which reach values of 30-46 µgPM_{10}/m^3 and 20-30 µg$PM_{2.5}$/m^3 (Querol et al., 2007).

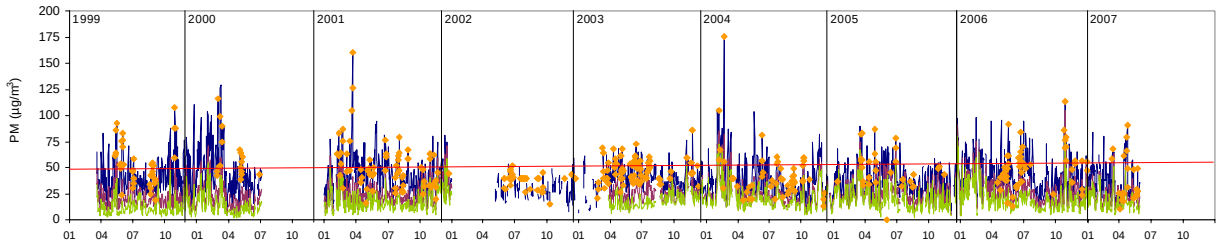

Figure 6.1. PM levels time series recorded at different sites in Barcelona from March 1999 to July 2007. Days with African dust outbreak influence are marked with yellow diamonds.

PM levels annual variation depends on the climatology and the frequency of African dust episodes in a year. There can also be temporal changes in anthropogenic emissions as road traffic and industrial emissions. In Barcelona, although mean annual levels of PM_{10} do not follow a definite trend, those of $PM_{2.5}$ and PM_1 tend to increase

from 1999 to 2006. It is not easy to attribute this upward trend exclusively to an increase in PM anthropogenic emissions given that data were obtained at different sites in Barcelona. Nevertheless, it should be noted that this trend is also observed for the 2003-2006 period when the measurements were carried out at the same site. In addition, the fact that the increasing trend is observed for the fine fractions but not for the coarser one suggests an anthropogenic origin. Thus, this increase could be related to the progressive rise in road traffic flow during the last decade and to the marked growth of the diesel fleet (from around 32% in 1999 to around 47% in 2005, Dirección General de Tráfico). However, 2007 data show a decrease compared with 2006, indicating that this 1999-2006 increasing trend at least is due in part to climatological causes. Figure 6.2 shows the mean PM_{10}, $PM_{2.5}$ and PM_1 levels from 1999 to 2007 in Barcelona for all days (total), days with African dust influence (NAF) and days without African dust influence (without NAF). Diesel fleet evolution is also shown from 1999 to 2005. These data has been obtained from the Dirección General de Tráfico website, http://www.dgt.es/estadisticas/estadisticas03.htm).

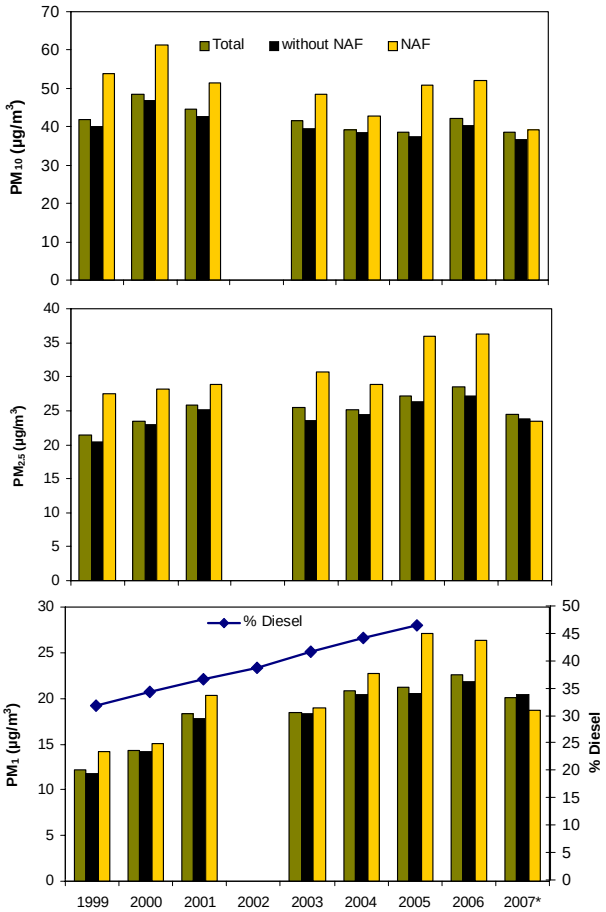

Figure 6.2. Mean annual PM levels from 1999 to 2007 for all days (total), days with African dust influence (NAF) and days without African dust influence recorded at Barcelona. Diesel fleet evolution in Spain (Dirección General de Tráfico).*2007 data only from January to July.

Montseny, as a regional background site presents lower PM levels than the urban background site at Barcelona. The mean PM levels recorded at Montseny during the period 2002-2007 are between the range of mean levels registered in other regional background sites in the Iberian Peninsula (15-20 $\mu gPM_{10}/m^3$ and 12-17 $\mu gPM_{2.5}/m^3$, Querol et al. 2004a y b y 2007).

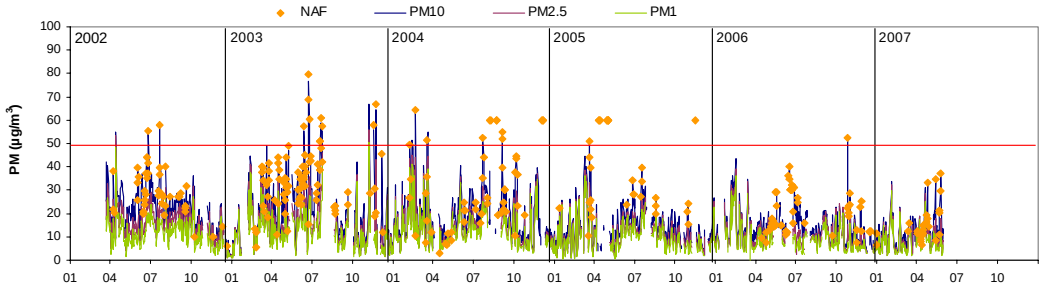

Figure.6.3. PM levels time series recorded at Montseny from March 2002 to June 2007. Days with African dust outbreak influence are marked with yellow diamonds.

Figure 6.4. Shows the mean annual PM_{10}, $PM_{2.5}$ and PM_1 levels measured at Montseny from 2002 to 2007 for all days (total), days with African dust outbreak influence (NAF) and days without African dust influence. PM levels follow a decreasing trend from 2002 to 2007, probably attributed to climatology, but this trend could also be caused by a variation of the anthropogenic regional load because of changes in the industrial emissions in the region.

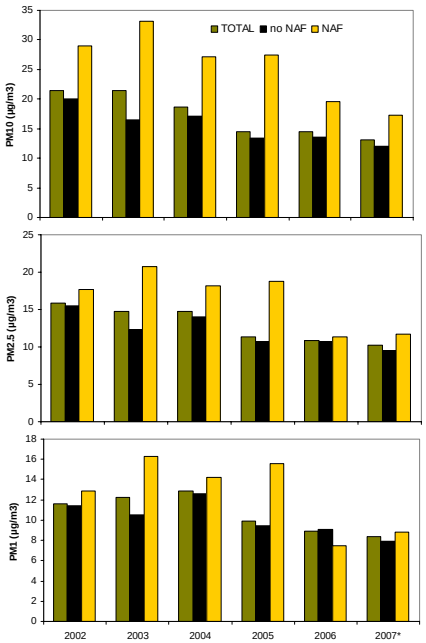

Figure 6.4. Mean annual PM levels from 2002 to 2007 for all days (total), days with African dust influence (NAF) and days without African dust influence recorded at Montseny. * 2007 data only from January to July.

6.1.2. Seasonal trends

Mensual mean PM_{10}, $PM_{2.5}$ and PM_1 levels registered at Barcelona from 1999 to June 2007 and at Montseny from 2002 to June 2007 are shown on Table 6.3.

Table 6.3. Mensual mean PM_{10}, $PM_{2.5}$ and PM_1 levels registered at Barcelona and Montseny from 1999 to June 2007.

	Barcelona-CSIC			Montseny		
	1999-2007			2002-2007		
$\mu g/m^3$	PM_{10}	$PM_{2.5}$	PM_1	PM_{10}	$PM_{2.5}$	PM_1
January	39	26	22	11	9	8
February	48	35	28	18	16	14
March	47	30	21	20	16	14
April	40	22	15	17	13	11
May	42	25	16	17	12	9
June	44	26	17	26	16	13
July	40	25	17	25	17	13
August	33	19	13	16	12	10
September	34	22	16	18	14	11
October	38	25	18	15	11	9
November	41	27	20	15	12	9
December	35	27	21	10	8	6

Figure 6.5. shows the monthly evolution of PM levels recorded from 1999 to 2007 at Barcelona. The highest levels are registered in winter (February and March). This maximum is related to the frequency of anticyclone situations in this area that favour the stagnation of pollutants near the emission sources. This situation can produce episodes of intense local pollution. The decrease in April is related to the higher rain rates and the Atlantic air mass advections registered during this month. The advective conditions produce air mass renovation. In addition they are usually coupled with rain that washes out the road dust from roads and diminishes resuspension. The summer increase (May to July) is associated with the higher frequency of African dust outbreaks, the recirculation of air masses that prevent the air renovation, the low precipitations registered, the higher resuspension due to the aridity of soils during this period and the formation of secondary aerosol from gaseous precursors caused by the stronger solar radiation (Querol et al., 2001, Viana et. al., 2002; Escudero et al., 2005). August presents the lowest levels in the year because of the lower traffic activity, being the usual holiday month in Spain. Then, the levels increase again from September to November because of the traffic activity, the anticyclonic situations and the occurrence of African dust outbreaks.

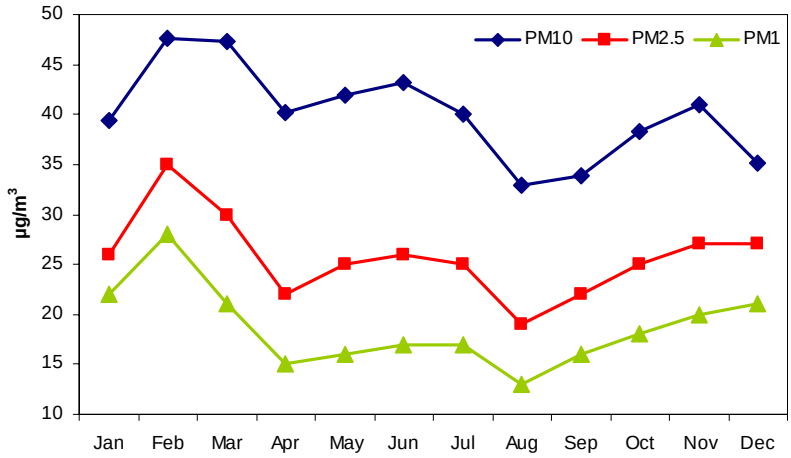

Figure 6.5. Monthly PM means registered at Barcelona from March 1999 to June 2007.

In Montseny the seasonal evolution of PM levels is markedly different from Barcelona (Figure 6.6). The highest levels are registered during the summer months (June and July). This summer maximum is related, as explained above for Barcelona, to the higher frequency of African dust outbreaks, the recirculation of air masses, the low precipitations, the higher resuspension and the formation of secondary aerosol. This summer increase is more pronounced in the coarse fraction ($PM_{10-2.5}$) than in the finer fractions ($PM_{1-2.5}$ and PM_1) because of the coarser size of the mineral dust particles associated to this type of episodes (Figure 6.7). The rest of the year the levels are low, except during winter months (February and March) when intense pollution episodes occur and the levels rise. These pollution episodes are related to the frequency of anticyclonic situations during this period, favouring the stagnation of pollutants in the pre-coastal depression (with industry and urban agglomerations) during several days. After a few days, the mountain winds, activated by solar radiation, push polluted air masses from the valley increasing the PM_{10} levels up to 40 µg/m^3. These pollution episodes are characterized by a fine PM grain size (Figure 6.7). During winter, African dust outbreaks can also occur contributing to increase PM levels (Escudero et al., 2005). The seasonal PM concentration variation at Montseny is also related to the boundary layer thickness variation. Montseny, at 700 m.a.s.l. during some periods in the winter can be situated outside of the boundary layer and be then less affected by the anthropogenic emissions than during summer, when it is inside the boundary layer.

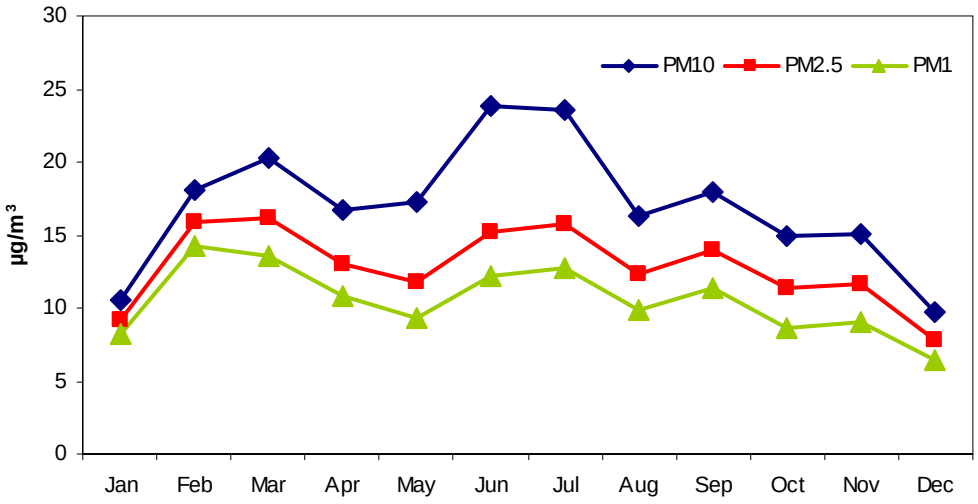

Figure 6.6. Monthly PM means registered at Montseny from March 2002 to June 2007.

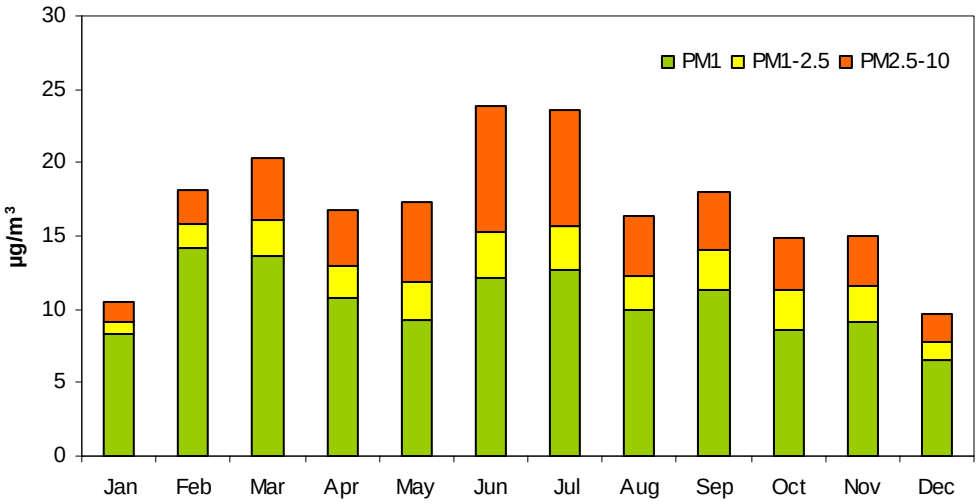

Figure 6.7. Monthly PM grain size partitioning registered at Montseny from March 2002 to June 2007.

6.1.3. $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios

The mean daily $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios obtained at Barcelona from 1999 to 2007 are shown in Figure 6.8. The ratios measured depended on the study site and the sources affecting PM levels. In the period 1999-2000, measured in L'Hospitalet site, the ratios were lower than in the rest of the sites, probably due to the proximity to road traffic. La Sagrera site in 2001 and Barcelona-CSIC site from 2003 to 2007 present higher ratios in general, reflecting the urban background environments.

$PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios show a seasonal trend, with minimums in summer, when the mineral dust influence is higher because of a higher resuspension and frequency of African dust episodes, and maximums during winter, with a finer PM distribution in general. The decrease in ratios is more marked for the PM_1/PM_{10} than for the $PM_{2.5}/PM_{10}$ ratio, probably because PM_1 is less affected by the mineral dust contributions from African dust or soil resuspension and presents a lower seasonal variation. The influence of African dust episodes on $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios is clearly shown in 2003, with a very warm and dry summer and a higher frequency of African dust outbreaks than the rest of the years. The ratios decrease more markedly for the 2003 summer than for the rest of the summers due to the higher input of coarse particles by the mineral dust.

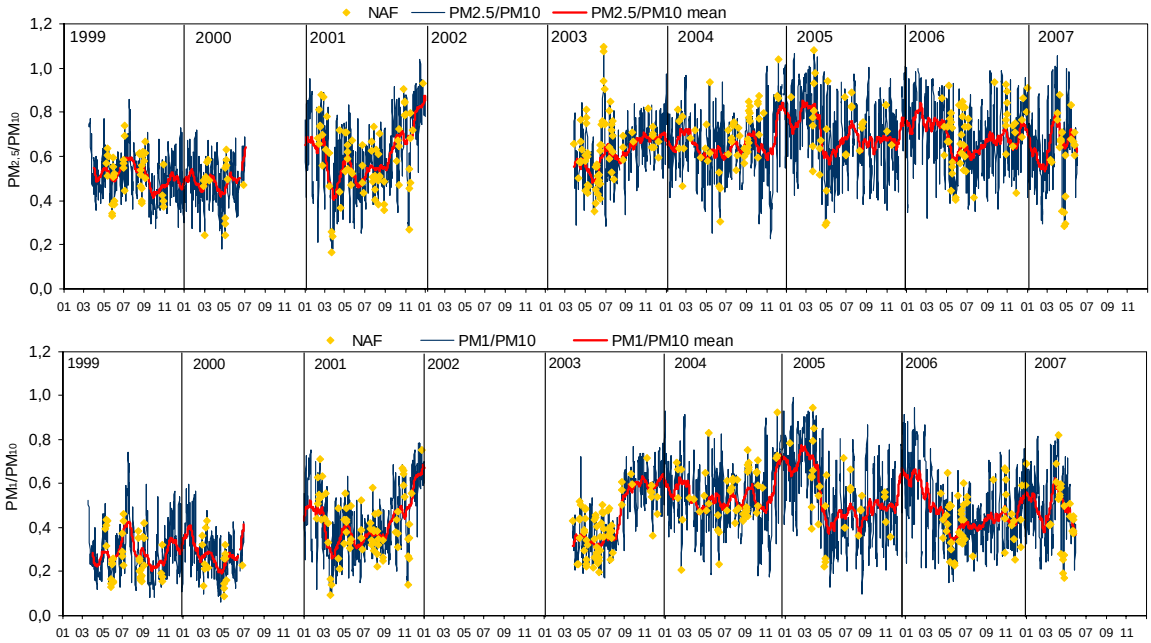

Figure 6.8. Ratios $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} in Barcelona from 1999 to 2007. The days with African outbreaks (NAF) and the sliding average for 30 days were marked.

In Montseny (Figure 6.9) the seasonal trend of the PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ ratios is the similar to the one discussed for Barcelona. The ratios follow a clear seasonal variation with maximums in winter and minimums in the summer. In 2003 (heat wave) and 2006 the decrease in the ratios during the summer is more marked than for the rest of the years. This is attributed to the warmer and drier summers and to the high frequency of African dust outbreaks during these two years.

In Montseny the ratio $PM_1/PM_{2.5}$ decreases more markedly during the summer months than the ratio $PM_{2.5}/PM_{10}$. This is due to the fact that the dust fraction from the soil

resuspension is present mainly in the range size PM_{10} and $PM_{2.5}$ and a very little fraction is present in PM_1.

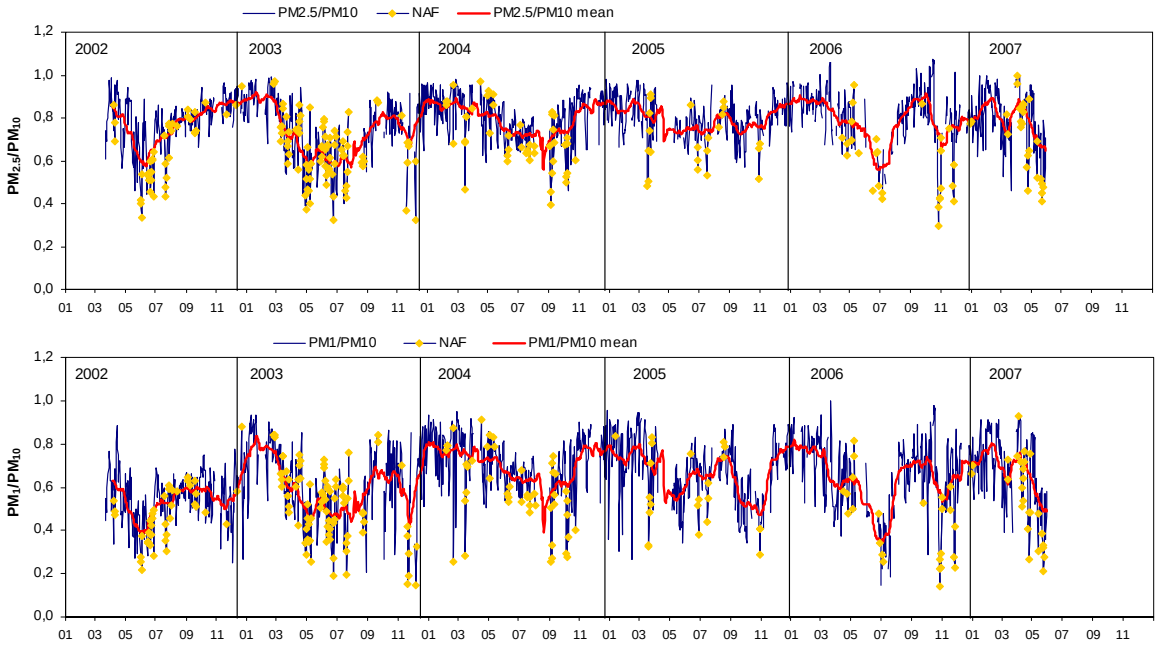

Figure 6.9. Ratios $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} in Montseny from 2002 to 2007. The days with African outbreaks (NAF) and the sliding average for 30 days were marked.

The $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios measured are higher for Montseny than for Barcelona (Figure 6.10). This is caused by the proximity of the anthropogenic emissions in Barcelona, causing a coarser size distribution, whereas at Montseny PM is transported with the consequent segregation of PM to the fine fraction.

Montseny presents a higher seasonal variability than Barcelona (Figure 6.10), attributed to the differences in soil resuspension during the summer and the winter and the intense pollution episodes occurring during the winter at Montseny. At Montseny during the summer a higher coarse fraction arising from resuspension and a higher frequency of African dust outbreaks lowers the PM ratios. During the winter the pollution with a fine grain size distribution that reaches the Montseny site increases the PM ratios. In contrast, $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios are more stable at Barcelona because of the high influence of road traffic resuspension that is observed during all the year.

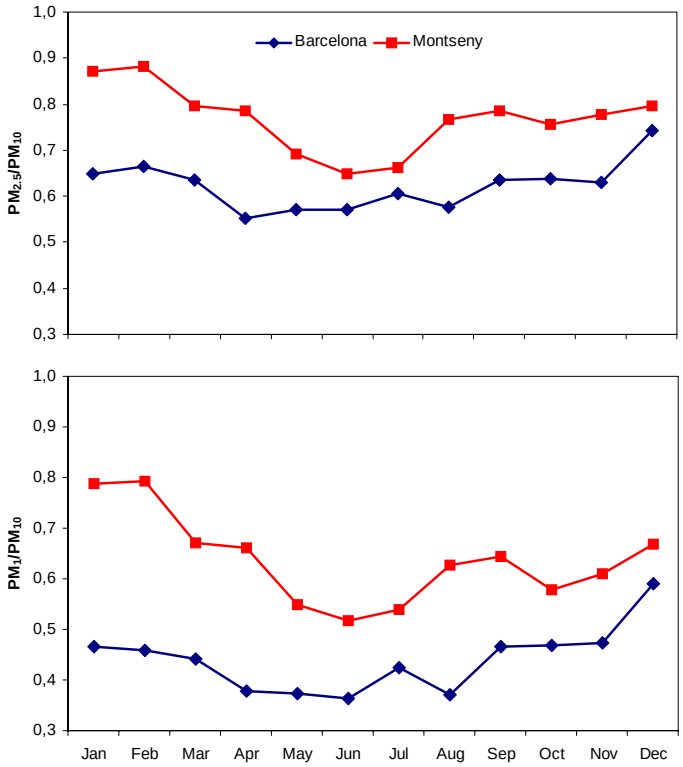

Figure 6.10. Ratios $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} measured at Barcelona (1999 to 2007) and Montseny (2002 to 2007).

6.1.4. Daily cycles

PM levels daily cycles at Barcelona urban background site are very influenced by traffic. PM_{10}, $PM_{2.5}$ and PM_1 levels show a maximum during morning traffic peak hours (Figure 6.11). This maximum is attributed to road dust resuspension and vehicle exhaust emissions (carbonaceous compounds or NO and SO_2 that are precursors of secondary inorganic compounds). The morning peak is more marked for PM_{10} than for the finer fractions because road dust falls mainly in the coarse size range and thus road dust resuspension has a higher impact on PM_{10} levels. After peak traffic hours, the levels decrease as a consequence of atmospheric dilution processes and deposition of the coarser particles. At night, when the traffic activity is lower, the emissions decrease ant it is reflected on PM_{10} levels. $PM_{2.5}$ and PM_1 do not follow the same pattern than PM_{10}. The finer particles have a longer residence lifetime in the atmosphere and their levels are affected by secondary particles that are formed after traffic peak hours from precursor gases emitted by vehicles. An increase is even observed for $PM_{2.5}$ and PM_1 levels at late hours (22 to 2 local time). This is due to the compression of the boundary layer during the night that makes concentration of pollutants increase and to the lower dilution processes (Viana et al., 2005; Allegrini et al., 1994).

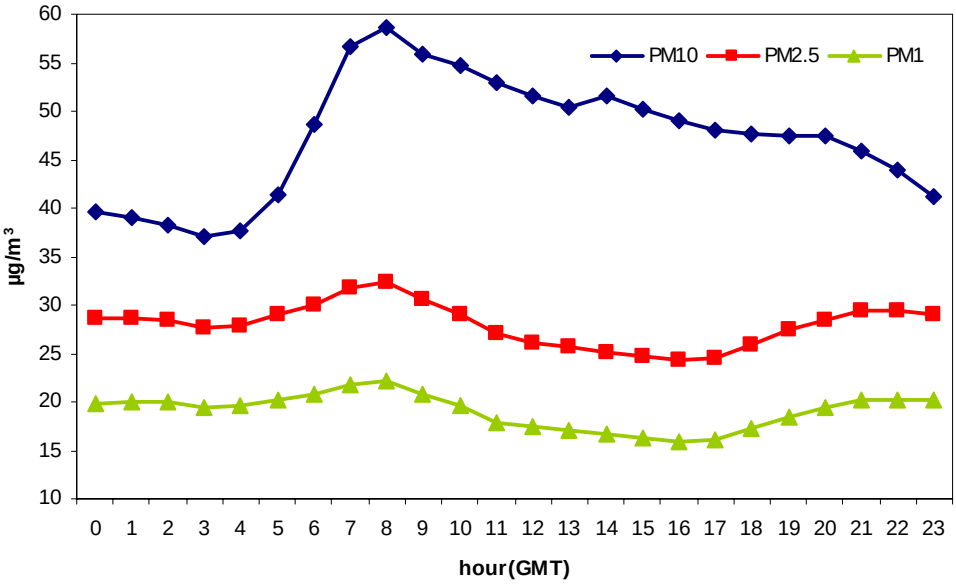

Figure 6.11. Mean PM daily cycles recorded at Barcelona-CSIC site during 2006.

PM levels daily cycle in Montseny follows a very different pattern than in Barcelona (Figure 6.12) the maximum PM_{10}, $PM_{2.5}$ and PM_1 levels being reached in the afternoon. The daily evolution of PM levels at Montseny depends strongly on the breeze system (mountain and sea breezes) that dominates the atmospheric dynamics at this site. During the night, relatively low PM levels are recorded, increasing progressively from early morning (6-8 h GMT in summer, 9-10 h GMT in winter) to the afternoon when they reach the highest values (12-14 h GMT in summer, 15-17 h GMT in winter). Then, the levels decrease progressively. This behaviour has already been observed by Castillo (2006). Pollutants are accumulated in the main valley (Vallès industrial area) and during the day the mountain and sea breezes bring air masses from the valley activated by insolation and make the PM levels rise. In the summer the breeze is more intense and is activated earlier (6-8 h GMT) and as a result the PM peak appears earlier than in the winter.

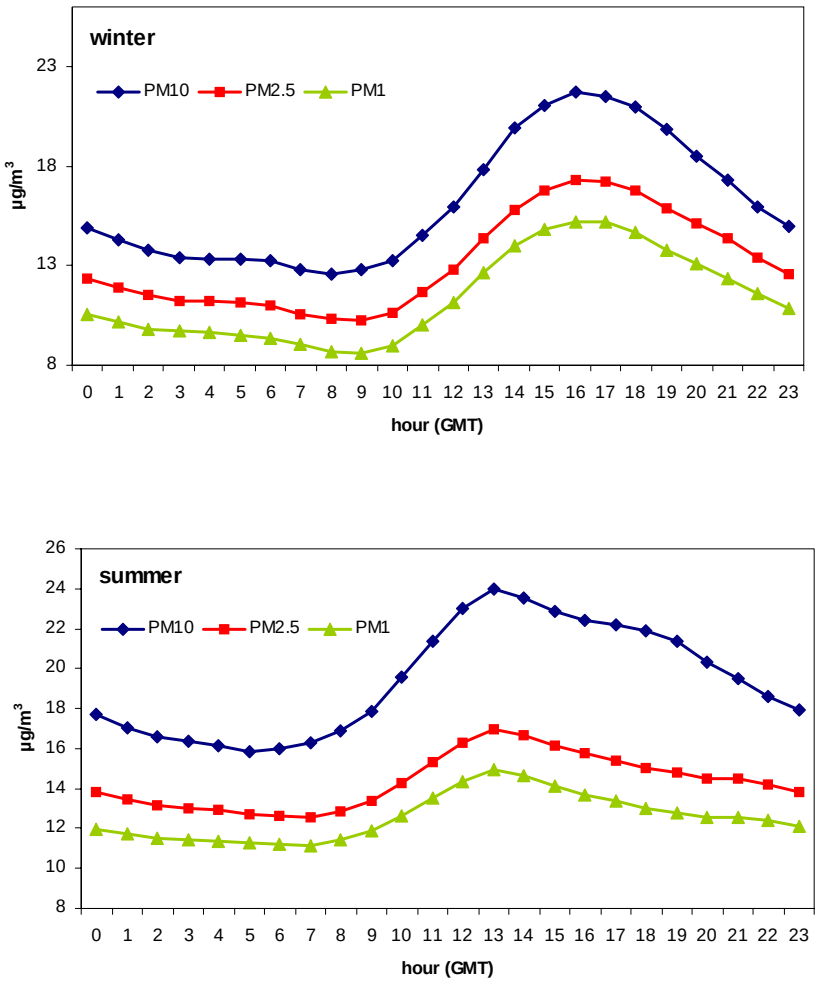

Figure 6.12. Mean PM daily cycles recorded at Montseny site during winter and summer from 2003 to 2005.

6.1.5. Influence of air mass origin on PM levels

Air mass origins are estimated by calculating mass back-trajectories, together with the study of satellite images and aerosol maps. In Figure 6.13, the annual relative frequencies for the different air mass origins considered for the region of this study are shown. The predominant origin is the Atlantic, especially the Western (WA) and North-western Atlantic (NWA). This is the result of the Azores anticyclone influence that favours the Western and North-western winds over the Iberian Peninsula. These observations are in accordance with the study carried out by Jorba et al. (2004) describing the synoptic transport patterns in Barcelona by cluster analysis of back-trajectories and describing almost a 50% of the analyzed situations to be Atlantic flows. The North-African (NAF) origin is also very frequent but it depends on the year, being

more important in 2001, 2003 and 2006. Regional (REG) are also very frequent being more important during 2005. Finally European and Mediterranean origins present a lower frequency.

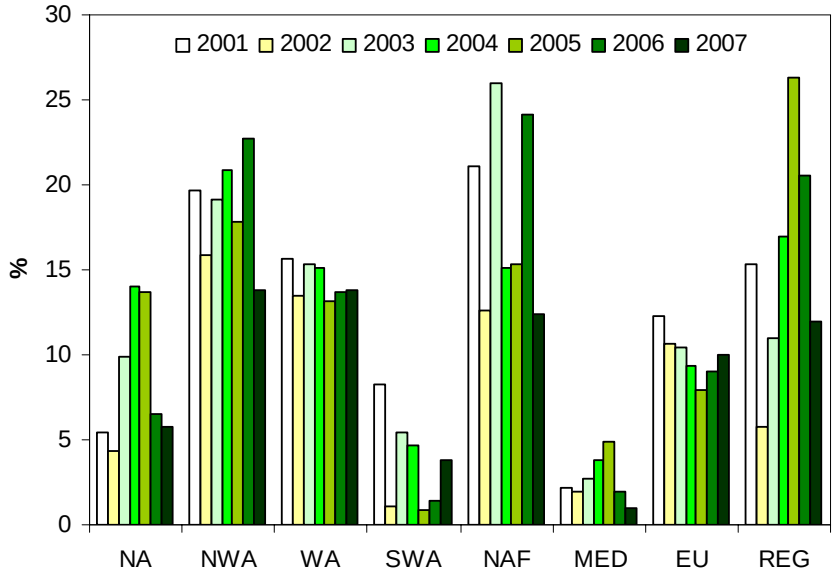

Figure 6.13. Annual relative frequencies of each air mass origin selected for the study region for the period 2001-2007.

Air mass origin influences the levels of PM, increasing the levels when the air transports particles from distant areas or decreasing them by the renovation of the air masses. The mean levels associated to each of the air mass origin are shown in Table 6.4 and Figure 6.14.

Table 6.4. Mean levels for each air mass origin considered in Barcelona (2001 to 2007) and Montseny (2002 to 2007).

	µg/m^3	NA	NWA	WA	SWA	NAF	MED	EU	REG
Barcelona	PM_{10}	33	35	38	42	46	33	41	44
	$PM_{2.5}$	21	22	24	26	31	26	28	29
	PM_1	16	17	17	19	22	20	22	23
Montseny	PM_{10}	14	15	14	14	25	15	18	18
	$PM_{2.5}$	11	12	11	11	16	12	15	14
	PM_1	9	10	9	9	13	10	12	12

The highest PM levels are observed for North African air mass origin at Barcelona and Montseny. North African air masses loaded with mineral dust increase PM levels, especially in the coarser fractions. PM_1 levels do not have an important variation with NAF, EU or REG episodes. In contrast, $PM_{2.5}$ and PM_{10} levels are clearly higher for

NAF than for REG or EU episodes. This is due to the coarser size contribution of North African dust to PM levels. In Montseny, a regional site with low PM levels in general, the increase in PM levels produced by these episodes is clearly distinguished. In areas with higher anthropogenic emissions like Barcelona the increase in PM levels by NAF episodes is also evident but it is less significant.

The regional recirculation episodes (REG) present also high PM levels that are associated to the accumulation and recirculation of pollutants over the region. Sometimes these episodes last a few days producing the aging of air masses. Aged air masses carry secondary aerosols (mainly ammonium sulphate) with a fine grain size. This explains that PM_1 levels in REG episodes present even higher levels than during NAF episodes.

The lowest PM levels are observed for Atlantic air mass advections and Mediterranean origin episodes, both at Barcelona and Montseny. These air mass advections renovate the air masses cleaning the atmosphere from pollutants and generally reducing PM levels. Sometimes Atlantic advections are associated with precipitations that contribute to wash out the suspended particles and to minimize the dust resuspension. Mediterranean episodes are also frequently associated to intense precipitations.

The European episodes are associated to strong winds that allow the renovation of air masses but sometimes the transport of pollutants from Central and Eastern Europe contributes to increment PM levels, especially the finer fractions because the air masses transported are charged with anthropic pollutants (mainly ammonium sulphate and nitrate).

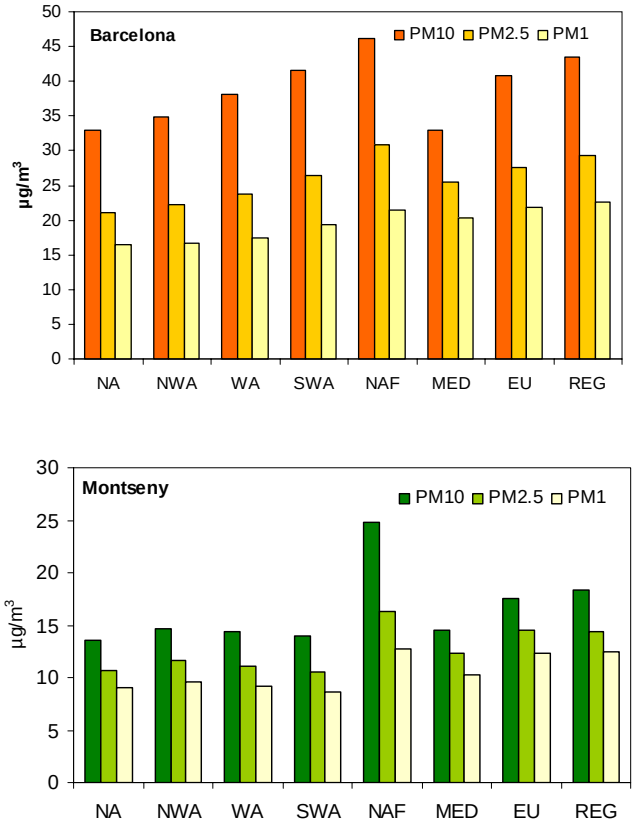

Figure 6.14. Mean PM levels by air mass origin registered at Barcelona (2001-2007) and Montseny (2002 to 2007).

6.1.6. Influence of African dust outbreaks on PM levels

The contribution of African mineral dust to the annual PM levels depended on the frequency and intensity of African outbreak episodes in a year. The annual number of days with clear African dust contribution varies widely. In the region studied, for the period 1999-2006 the number of African days varied from 32 (2005) to 85 (2003), with a mean value of 52 days (Table 6.5).

The influence of African dust outbreaks is more relevant as far as the daily increase of PM levels is concerned. The evaluation of the measured data shows that daily African dust contributions to PM_{10} higher than 25 µg/m^3 (and up to 60µg/m^3) are usually reached a few days every year. Dust outbreaks may contribute to exceed the 50 µgPM_{10}/m^3 daily limit level. For the period 1999-2006 in Barcelona, the annual daily exceedances of the 50 µgPM_{10}/m^3 daily value were between 63-104 and the 35 µg$PM_{2.5}$/m^3 daily value was exceeded between 23-97 days. Of these days, between 10-30 (16-45%) for PM_{10} and 3-27 (13-65%) for $PM_{2.5}$ were recorded during days with African dust influence. Between 36-77 (55-84%) of the daily exceedances for PM_{10} and 9-70 (35-87%) for $PM_{2.5}$ were due exclusively to anthropogenic activity. Most of the

exceedances recorded during days with African dust influence in Barcelona are not attributed exclusively to natural causes, being the anthropogenic mineral load dominant.

In Montseny the 50 µgPM_{10}/m^3 daily limit value was exceeded between 1 (2006) and 9 (2003) times in a year and the 35µg$PM_{2.5}$/m^3 daily limit value from 1 (2006) to 10 (2004) times considering the period from 2002 to 2006. The exceedances of the PM_{10} daily limit value recorded at Montseny occur almost in all cases during NAF episodes and can be attributed to the African dust contribution.

Table 6.5. Number of days with African dust influence in the study region. Number of exceedances of the 50 µgPM_{10}/m^3 daily limit value and % of the exceedances recorded during NAF episodes.

	NAF days number	Number of Exceedances of the daily limit level				% Exceedances during NAF			
		Barcelona		Montseny		Barcelona		Montseny	
		PM_{10}> 50µg/m^3	$PM_{2.5}$> 35µg/m^3	PM_{10}> 50µg/m^3	$PM_{2.5}$> 35µg/m^3	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
1999	48	72	26			29	35		
2000	33	63	23			16	13		
2001	71	102	64			27	25		
2002	40			3	1			67	0
2003	85	66	26	9	8	45	65	89	38
2004	56	74	60	7	10	18	20	71	30
2005	32	72	73	1	2	18	19	100	0
2006	53	104	97	1	1	26	28	100	0
2007*	29	35	18	0	0	17	6		

*2007 annual data incomplete. Not used in the calculations.

The difference between the PM mean annual levels and the mean levels obtained for days without African dust could be considered as the African dust contribution to PM (Table 6.6 and Figure 6.15).

At the Barcelona site, the annual increase of PM levels due to the African dust influence is around 0.6-2.3, 0.5-1.4 and 0.1-0.6 µg/m^3 (1.6, 1.0 and 0.4 mean values respectively) for PM_{10}, $PM_{2.5}$ and PM_1 measured in the period 1999-2006.. The highest African dust contribution to PM levels (2.3 and 1.8 and µg/m^3 for PM_{10} and $PM_{2.5}$ respectively) was recorded during the year 2003, in accordance with the highest frequency of dust outbreaks during this year.

In Montseny the annual increase of PM levels due to the African dust influence was around 0.8-4.9, 0.1-2.4 and 0.1-1.7 µg/m^3 (1.9, 0.8 and 0.5 mean values respectively) for PM_{10}, $PM_{2.5}$ and PM_1 during the period 2002-2006. The highest contribution is also

observed for the year 2003 (4.9, 2.4 and 1.7 µg/m^3 for PM_{10}, $PM_{2.5}$ and PM_1 respectively). These results are in accordance with previous studies carried out by Castillo (2006), where the mean annual contribution of North-African dust to PM_{10} was estimated to be between 1-2 µgPM_{10}/m^3 and 0.2-1 µg$PM_{2.5}$/m^3

Table 6.6. Mean PM annual levels at Barcelona (1999 to 2006 data) and Montseny (2002 to 2006 data). Mean annual levels for days without African dust influence (no NAF). Increase in the annual PM levels attributed to African dust outbreaks.

		PM mean annual levels (µg/m^3)	No NAF PM levels (µg/m^3)	Annual increase of PM related to NAF (µg/m^3)
Barcelona 1999-2006	PM_{10}	39-48	37-47	0.6-2.3
	$PM_{2.5}$	21-29	20-27	0.5-1.8
	PM_1	12-21	12-21	0.1-0.6
Montseny 2002-2006	PM_{10}	14-21	13-20	0.8-4.9
	$PM_{2.5}$	11-16	11-16	0.1-2.4
	PM_1	9-13	9-13	0.1-1.7

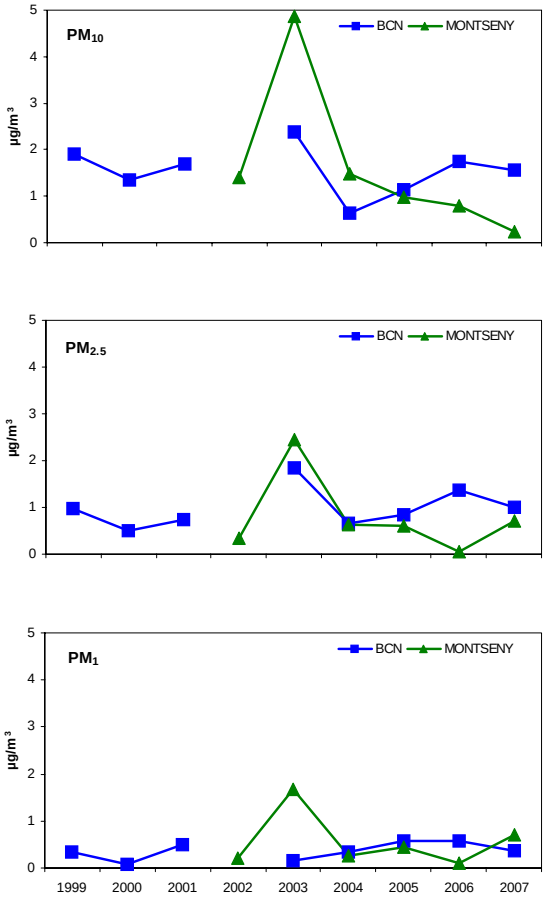

Figure 6.15. Annual increment of PM_{10}, $PM_{2.5}$ and PM_1 levels attributed to African dust outbreaks

PM_{10}, $PM_{2.5}$ and PM_1 levels are not affected by African dust outbreaks in the same extent. Mineral dust is mainly coarse in grain size and the increase in annual PM levels is more marked in PM_{10} than in the finer fractions.

African dust can be transported at different heights in the atmosphere depending on the meteorological scenario producing the African dust outbreak. The Montseny regional background site is situated at 720 m.a.s.l and the Barcelona site at 68 m.a.s.l. The two sites can sometimes be affected differently by African dust outbreaks, depending of the transport height of the air mass transporting the dust. This is the reason why the annual African dust contribution at Barcelona and Montseny can be slightly different.

6.2. PM speciation at Barcelona and Montseny

6.2.1. Barcelona

The results of the PM_{10}, $PM_{2.5}$ and PM_1 chemical speciation analysis performed at three different monitoring sites in Barcelona from 1999 to 2006 for are shown on Table 6.7. The results obtained for the fractions PM_{10} and $PM_{2.5}$ in the different sites show similar levels for the different components.

Table 6.7. Mean annual levels of PM_{10}, $PM_{2.5}$ and PM_1 and their major components registered at different sites of Barcelona between 1999 and 2006.

	PM_{10}			$PM_{2.5}$			PM_1
	CSIC [a] 2003-2006	Sagrera [b] 2001	L'Hospitalet [c] 1999-2000	CSIC [a] 2003-2006	Sagrera [b] 2001	L'Hospitalet [c] 1999-2000	CSIC [d] 2005-2006
µg/m^3	47.2	46.2	49.5	31.3	27.6	33.9	19.4
OM+EC	11.5	13.7	15.9	11.0	12.2	13.2	9.5
SO_4^{2-}	5.5	5.2	6.9	4.5	4.2	5.6	2.9
NO_3^-	5.1	3.9	5.8	3.0	2.2	4.0	1.7
NH_4^+	1.6	2.0	2.7	1.8	2.0	3.2	1.1
SIC	12.2	11.1	15.4	9.3	8.4	12.8	5.8
Crustal	14.5	15.2	12.9	5.1	4.2	3.8	0.9
Marine	1.9	2.4	2.3	0.7	0.7	0.8	0.2
Unaccounted	7.1	3.8	3.0	5.3	2.1	4.2	3.2

[a] Annual mean, this study. [b] Annual mean, Querol (2004a). [c] Annual mean, Querol et al. (2001) and Rodríguez et al. (2003). [d] Annual mean, this study. ND. Not determined.

The speciation analysis of PM_1 was carried out at Barcelona only from October 2005. For the study of the speciation data I have selected the period October 2005 to October 2006, when the simultaneous chemical speciation analysis of the three PM fractions

(PM_{10}, $PM_{2.5}$ and PM_1) is complete. Bearing this in mind, the partitioning of PM components in the $PM_{2.5-10}$ $PM_{1-2.5}$ and PM_1 fractions is described below using the simultaneously obtained data on PM_{10}, $PM_{2.5}$ and PM_1 during 2005-2006 (Table 6.8 and Figure 6.16).

Table 6.8. Mean levels of PM_{10}, $PM_{2.5}$ and PM_1 and their major components registered at Barcelona-CSIC from October 2005 to October 2006. ND: Not determined.

	PM_{10}	$PM_{2.5}$	PM_1
$\mu g/m^3$	44.9	29.4	19.1
OM+EC	10.1	10.2	8.7
SO_4^{2-}	5.2	4.6	3.3
NO_3^-	5.1	2.7	1.5
NH_4^+	1.1	1.4	1.2
SIC	11.4	8.6	2.7
Crustal	14.6	4.8	0.9
Marine	2.0	0.5	0.2
Unaccounted	6.7	5.3	3.4

Composition of the fractions PM_{10}, $PM_{2.5}$, $PM_{2.5-10}$ $PM_{1-2.5}$ and PM_1

The coarse fraction ($PM_{2.5-10}$) was mainly made up of mineral dust (63%) and marine aerosol (10%) although proportions of coarse SIA (Na, Ca, K, Mg sulphates and nitrates) were also present (20-25%). The carbonaceous material was found at very low levels in this fraction.

The mass of marine aerosol and that of mineral dust were reduced in the $PM_{2.5}$ (2 and 16% respectively) with respect to the PM_{10} (5 and 32% respectively). Most of the carbonaceous components present in PM_{10} also fall within the $PM_{2.5}$ range (almost no OM+EC is present in the $PM_{2.5-10}$ fraction) but, as stated above a fraction of the SIA, particularly nitrate, was coarse, and consequently not present in $PM_{2.5}$. Thus $PM_{2.5}$ was still a mixture of SIA (30%), carbonaceous material (38%) and a large proportion of mineral dust (16%). The mineral load in $PM_{2.5}$ continues to be high given the influence of primary PM emissions at urban sites.

The mineral matter load in PM_1 (5%) was much more reduced than in $PM_{2.5}$ (16%). Around 80% of the carbonaceous material present in $PM_{2.5}$ continued to be found in PM_1. However, concentrations of SIA (especially nitrate levels) were reduced by 20-30% in PM_1 with respect to $PM_{2.5}$. Thus, the $PM_{1-2.5}$ fraction was made up of mineral dust (38%) and SIA (27%), with a fraction of carbonaceous matter (24%). The PM_1 fraction was predominantly made up of OM+EC (46%), SIA (31%) and minor proportions of mineral dust and marine aerosol.

Partitioning of PM components in the $PM_{2.5-10}$, $PM_{1-2.5}$ and PM_1 fractions

The partitioning of *crustal components* was 6/27/67% for $PM_1/PM_{1-2.5}/PM_{2.5-10}$, respectively. As stated above, the high mineral dust load arises mainly from anthropogenic emissions, such as road dust resuspension, demolition and construction. Dust accumulation on roads is favoured by the relatively long periods without rain in this region. A lower contribution is attributed to African dust events and natural resuspension from arid soils, but as previously stated this may be very high during these episodes.

The *marine aerosol* is mainly coarse. The partitioning was 8/15/77% for $PM_1/PM_{1-2.5}/PM_{2.5-10}$, respectively. A significant fraction is still present in $PM_{2.5,}$ but markedly diminished in PM_1.

Carbonaceous material (organic matter and elemental carbon) was mainly present in the fine fraction (78/22/<5% in the $PM_1/PM_{1-2.5}/PM_{2.5-10}$ fractions, respectively). In this urban environment, the carbonaceous material is mainly anthropogenic, emitted by road traffic and in a minor proportion by power stations, specific industrial processes, biomass combustion and biogenic emissions.

Sulphate was distributed among the three PM fractions with a fine grain size (63/26/11% in the $PM_1/PM_{1-2.5}/PM_{2.5-10}$ fractions, respectively) as a consequence of the prevalence of ammonium sulphate (fine aerosols) versus the coarser Ca, Na or Mg sulphate species.

Nitrate was distributed among the three PM fractions with a shift towards the coarse fraction (30/22/48% in $PM_1/PM_{1-2.5}/PM_{2.5-10}$, respectively). The fine size fraction is due to the presence of fine ammonium nitrate, but coarser Na and Ca nitrates also occur in appreciable levels.

Ammonium showed a fine size distribution (80/20% in the $PM_1/PM_{1-2.5}$ fractions respectively) as a consequence of the fine grain size of ammonium sulphate and nitrate. Most of the ammonium present in PM_{10} also falls in the $PM_{2.5}$ range. On occasions lower concentrations are observed in PM_{10} than in $PM_{2.5}$. This behaviour was observed in urban areas and has been attributed to a negative artefact due to the volatilization of NH_4Cl by the reaction of NH_4NO_3 with NaCl on the PM_{10} filter (Querol et al, 2001).

The *unaccounted mass* followed a size distribution very similar to that reported for nitrate and sulphate (62/17/21% in $PM_1/PM_{1-2.5}/PM_{2.5-10}$, respectively). These species are very hydrophilic and tend to accumulate water (the main cause of the unaccounted mass).

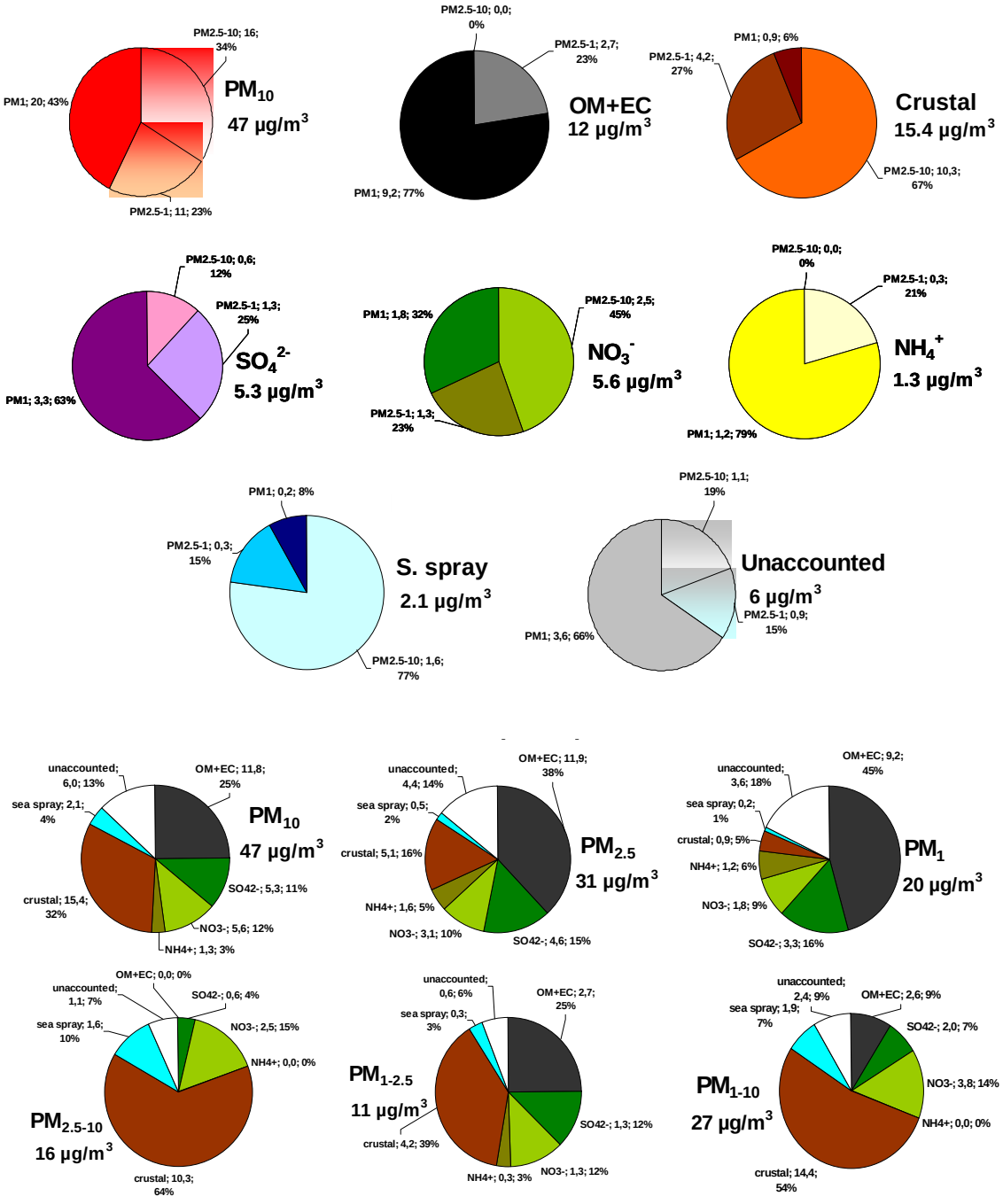

Figure 6.16. Mean composition of PM_{10}, $PM_{2.5}$ and PM_1 at the Barcelona-CSIC site, from 10th October 2005 to 6th October 2006.

Trace elements

The mean levels of trace elements (including metals) measured at Barcelona-CSIC in 2003-2006, at Sagrera in 2001 and at L'Hospitalet in 1999-2000 are shown in Table

6.9. The elements studied do not present a large time and spatial variation in the Barcelona metropolitan area, with a few exceptions such as Zn (higher contents in L'Hospitalet) and Pb (higher contents before 2001 when unleaded petrol became obligatory).

The levels of trace elements did not exceed the limit and target values of the CE standards (2004/107/CE y 1999/30/CE). However, as shown in Figure 5.17, the levels of V and Ni (mainly due to fuel oil combustion) and Mn, Cu, Zn, Sb and Li (mainly attributed to road dust) recorded in Barcelona are in the upper range of the concentrations registered at urban background sites with low industrial influence in Spain (Querol et al., 2007).

Table 6.9. Mean levels of trace elements in PM_{10}, $PM_{2.5}$ and PM_1 registered in different sites at Barcelona between 1999 and 2006.

	PM_{10}			$PM_{2.5}$			PM_1
	CSIC [a]	Sagrera [b]	L'Hospitalet[c]	CSIC [a]	Sagrera [b]	L'Hospitalet[c]	CSIC [d]
ng/m^3	2003-2006	2001	1999-2000	2003-2006	2001	1999-2000	2005-2006
Li	0.6	0.7	ND	0.3	0.2	ND	0.1
P	30	32	44	14	19	30	5
Ti	45	84	54	17	26	16	1.8
V	12	15	13	9	10	9	6
Cr	6	8	6	3	3	6	1.2
Mn	20	23	24	10	10	14	4
Co	0.4	0.4	ND	0.2	0.3	ND	0.1
Ni	6	7	7	4	5	6	3
Cu	80	49	74	43	31	52	12
Zn	103	98	263	69	55	191	48
As	1.1	1.5	ND	0.8	1.0	ND	0.6
Se	0.9	1.1	ND	0.6	0.8	ND	0.3
Rb	1.3	1.8	ND	0.5	0.7	ND	0.2
Sr	6	6	7	2	2	4	0.9
Cd	0.5	0.7	ND	0.4	0.6	ND	0.3
Sn	6	4	ND	3	4	ND	2
Sb	7	10	ND	3	4	ND	0.9
Ba	27	41	38	12	9	23	9
La	0.4	0.6	ND	0.2	0.2	ND	0.1
Ce	0.9	1.3	ND	0.4	0.5	ND	0.2
Tl	0.3	0.3	ND	0.2	0.3	ND	0.1
Pb	26	58	149	19	40	130	17
Bi	0.6	0.4	ND	0.4	0.2	ND	0.2
Th	0.1	0.3	ND	0.1	0.2	ND	0.1
U	0.1	0.2	ND	0.1	0.3	ND	0.1

[a]Annual mean levels, Querol et al. (2004 and 2007) and PhD. thesis of J. Pey y N. Pérez. [b]Annual mean, Viana (2003) and Querol (2004 and 2007). [c]Annual mean, Querol et al. (2001), Rodríguez (2002) and Rodríguez et al. (2003). [d]Annual mean, non published data, PhD thesis N. Pérez. ND: Not determined

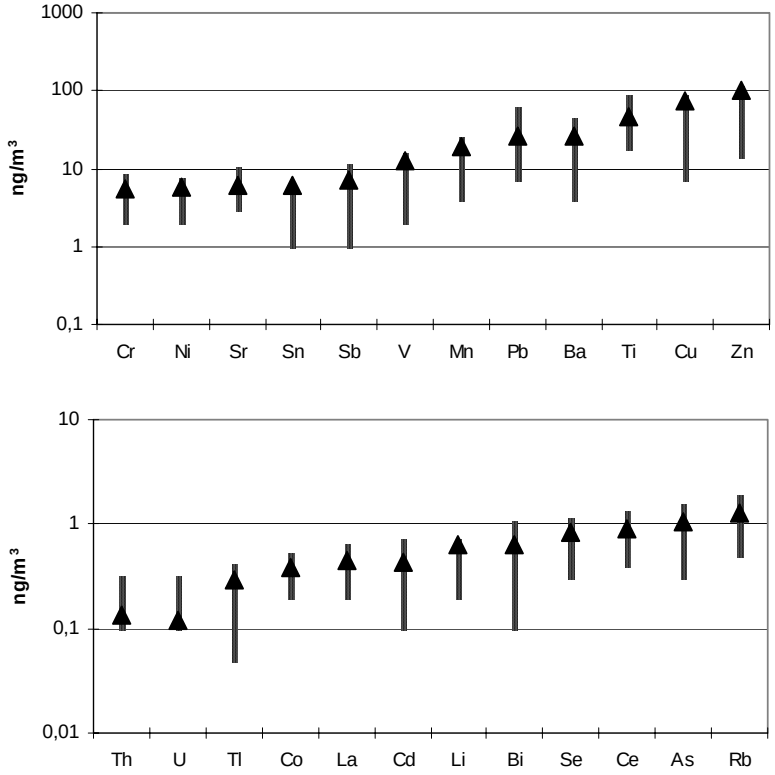

Figure 6.17. Mean levels of trace elements in PM_{10} at the CSIC site in Barcelona for 2003-2006 compared with the concentration ranges registered at other urban background sites with a low industrial influence in Spain (Querol et al., 2007).

The trace elements showed a clear partitioning trend between the PM_{10-1} and the PM_1 fraction, probably reflecting the origin of some of these elements. Figure 6.18 shows the ratios PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ for the elements analysed. Elements associated with fossil fuel combustion (V, Ni) or other high temperature industrial processes (As, Cd, Pb and U) occur in very fine particles (50 to 82% in the PM_1 fraction). Other elements usually associated with mineral matter emitted by road dust, construction and/or demolition, such as Ti, Li, Rb, Sr, La, Ce, P, and Th, or with road traffic abrasion products (mainly from tires and brakes) such as Sb, Cu, Mn, Cr, Co, Sn, Tl, Ba, Bi, Se, and Zn, (Wahlin et al., 2006, Schauer et al., 2006) tend to accumulate in the coarse mode (68 to 95% in the fraction PM_{10-1}).

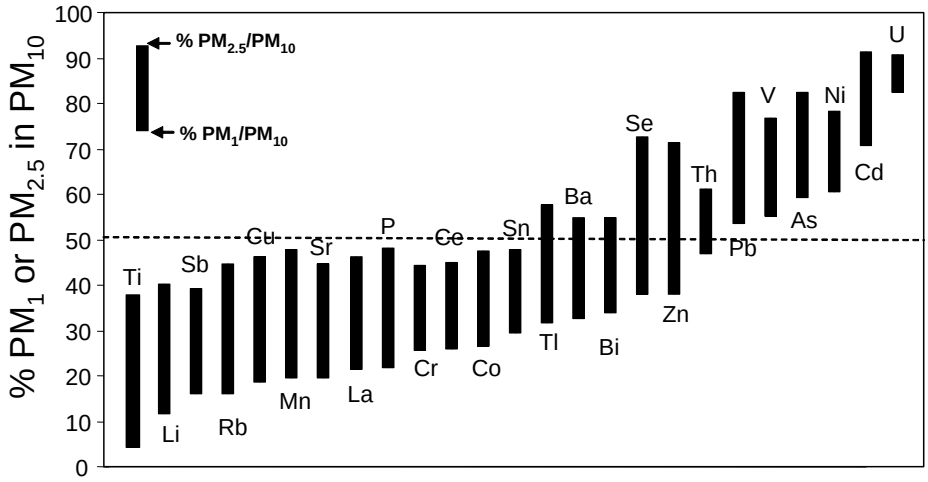

Figure 6.18. Mean $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios for levels of trace elements at the Barcelona-CSIC site, from October 2005 to October 2006.

Seasonal evolution of PM components at Barcelona

The PM components measured at Barcelona show a clear seasonal trend. The mean annual cycle of the main PM components measured at Barcelona from 2003 to 2006 is shown in Figure 6.19.

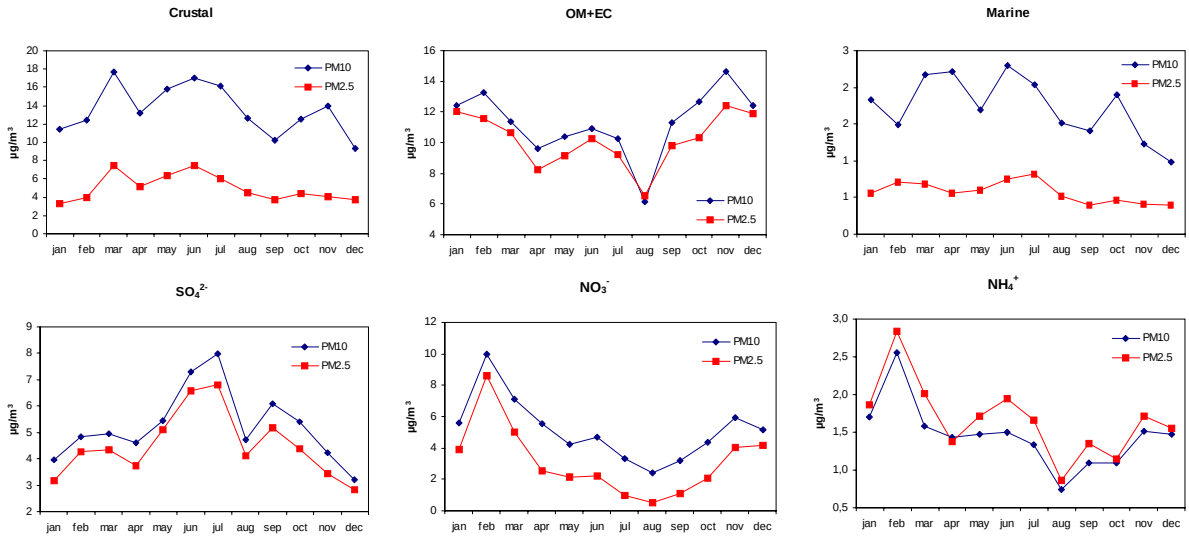

Figure 6.19. Mean annual cycle of the main PM components measured at Barcelona from 2003 to 2006.

The crustal material presents a clear seasonal trend. During the winter the levels of crustal material are low because of the humidity and precipitations that prevent dust resuspension. The highest levels are registered in March and are related to the occurrence of African dust outbreaks during this month. Then, in April the levels decrease again due to the high frequency of precipitations during this month. The levels of crustal material are high during all the summer (May, June and July) associated to a higher soil resuspension because of a lower precipitation rate and also

to the frequency of African dust outbreaks. In August and September the levels decrease because of the lower traffic intensity and the occurrence of precipitations. Then, in October and November, the levels increase again, also associated to the occurrence of African dust outbreaks during this period of the year.

The carbonaceous compounds (OM+EC) present the maximum levels during the winter months, associated to the strong pollution episodes recorded in this period of the year due to the atmospheric stability. The minimum levels are presented in April, related to the higher precipitation rates, and August, because of the lower traffic intensity during this month.

The concentration of the sea spray shows three maximums along the year: March-April, June-July and October. This behaviour could be associated to the breezes transporting the sea spray and depend on the main atmospheric scenarios occurring over Barcelona during the year.

Sulphate levels present a maximum in the summer related to the higher oxidation rate of the SO_2 due to a stronger insolation and thus a higher photochemical activity during summer months.

Nitrate levels show an inverse relationship with sulphate. The levels are maximum in winter and minimum in summer. This is due to the thermal instability of ammonium nitrate.

Ammonia presents high levels during the winter months associated to the stability of ammonium nitrate. During the summer ammonium nitrate is not stable but ammonia concentration presents a peak that is due to the formation of ammonium sulphate.

6.2.2. Montseny

The speciation of PM_{10} and $PM_{2.5}$ at Montseny was performed simultaneously from october 2003. Until this date, TSP was sampled instead of PM10. For this study I will present the PM_{10} and $PM_{2.5}$ simultaneous data from 2004 to 2006 (Table 6.10). The composition of PM_{10} and $PM_{2.5}$ and partitioning of PM components between the $PM_{2.5-10}$ and $PM_{2.5}$ fractions is described below using the PM_{10} and $PM_{2.5}$ chemical speciation measured during 2004-2006 (Figure 6.20).

Table 6.10. Levels of PM_{10}, $PM_{2.5}$ and their major components registered at Montseny from 2004 to 2006. ND. Not determined.

	PM_{10}			$PM_{2.5}$		
	2004	2005	2006	2004	2005	2006
$\mu g/m^3$	20.5	16.4	15.1	18.8	12.4	13.4
OM+EC	3.6	3.4	3.4	3.3	3.8	3.7
SO_4^{2-}	2.9	2.8	2.3	3.0	2.7	2.8
NO_3^-	2.0	1.9	1.5	1.7	1.3	1.3
NH_4^+	1.2	1.4	0.6	1.4	1.5	0.9
SIC	6.0	6.1	4.4	6.0	5.5	4.9
Crustal	5.4	3.7	4.1	2.3	0.9	1.4
Marine	0.7	0.6	0.4	0.2	0.3	0.2
Unaccounted	4.6	2.7	2.7	5.5	1.8	3.4

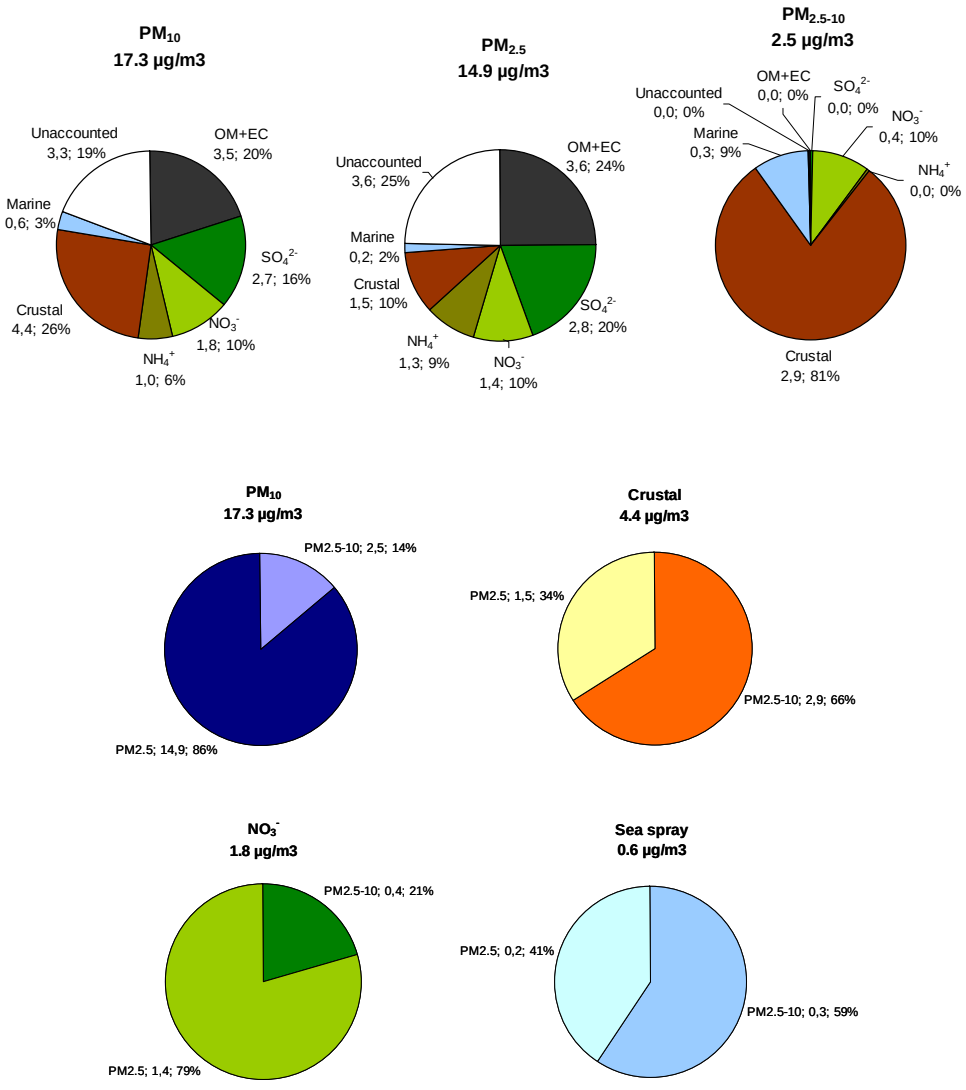

Figure 6.20. Mean composition of PM_{10} and $PM_{2.5}$ at Montseny from 2004 to 2006.

Composition of the fractions PM_{10}, $PM_{2.5}$ and $PM_{2.5-10}$ in Montseny

The coarse fraction ($PM_{2.5-10}$) was mainly made up of mineral dust (81%), marine aerosol (9%) and nitrates (10%). The carbonaceous material, ammonia and sulphate were found at very low levels in this fraction.

$PM_{2.5}$ was a mixture of SIA (40%), carbonaceous material (24%) and mineral dust (10%). The mass of marine aerosol (2%) and that of mineral dust (10%) were reduced in the $PM_{2.5}$ with respect to the PM_{10} (3 and 26% respectively). Most of the carbonaceous components present in PM_{10} also fall within the $PM_{2.5}$ range (almost no OM+EC is present in the $PM_{2.5-10}$ fraction). Most sulphate was also present in this fraction.

Partitioning of PM components in the $PM_{2.5-10}$, and $PM_{2.5}$ fractions

The partitioning of *crustal components* was 34/66% for $PM_{2.5}$/$PM_{2.5-10}$, respectively. Mineral dust load in a regional site has a natural origin and it is attributed to natural resuspension from arid soils and in a minor proportion to African dust events. Soil dust resuspension is favoured by the relatively long periods without rain in this region. African dust contribution to crustal levels can be very high during the occurrence of these events.

The *marine aerosol* was distributed among the two fractions with a shift towards the coarse fraction. The partitioning was 41/59% for $PM_{2.5}$/$PM_{2.5-10}$, respectively.

Carbonaceous material (organic matter and elemental carbon) was mainly present in the fine fraction (almost 100% in the $PM_{2.5}$ fraction). The carbonaceous material measured at a regional background site can be biogenic (secondary organic compounds, pollens and vegetal debris) or anthropogenic (biomass combustion).

Sulphate was mainly present in the $PM_{2.5}$ fraction as a consequence of the prevalence of ammonium sulphate (fine aerosols) versus the coarser Ca, Na or Mg sulphate species.

Nitrate was mainly in the $PM_{2.5}$ fraction. The partitioning was 21/79% for $PM_{2.5}$/$PM_{2.5-10}$, respectively. The finer size distribution is due to the prevalence of fine ammonium nitrate, but coarser Na and Ca nitrate also occur in appreciable levels.

Ammonium showed a fine size distribution. Almost all was present in the $PM_{2.5}$ fraction as a consequence of the fine grain size of ammonium sulphate and nitrate.

Trace elements

The mean levels of trace elements (including metals) measured at Montseny from 2004 to 2006 are shown on Table 5.11. The elements studied do not present a large time and spatial variation in the area.

The trace elements showed a clear partitioning trend between the $PM_{10-2.5}$ and the $PM_{2.5}$ fraction, probably reflecting the origin of some of these elements. Figure 6.21 shows the ratios $PM_{2.5}/PM_{10}$ for the elements analysed. Elements associated with mineral matter (Ti, Sr, Rb, Ce, Li, La) tend to accumulate in the coarse mode. The mineral matter origin at Montseny arises from arid soil resuspension and African dust outbreaks. Other elements occur in fine particles (Zn, Cu, U, Pb, Cr, Sn, Cd, Ni, As, Bi) and can be associated to anthropogenic emissions.

Table 6.11. Mean levels of trace elements in PM_{10} and$PM_{2.5}$ registered at Montseny between 2004 and 2006.

	PM_{10}			$PM_{2.5}$		
ng/m^3	2004	2005	2006	2004	2005	2006
Li	0.3	0.2	0.3	0.1	0.1	0.2
P	14.3	13.3	12.0	7.7	5.5	5.8
Ti	24.9	17.1	19.9	8.9	4.1	6.8
V	3.5	4.0	3.4	2.7	2.5	3.5
Cr	1.1	1.0	0.8	1.4	0.8	1.0
Mn	6.2	4.7	4.7	3.2	2.0	2.7
Co	0.2	0.1	0.1	0.1	0.1	0.1
Ni	1.7	1.8	1.5	2.0	1.5	1.8
Cu	9.6	4.7	5.2	9.6	6.2	10.1
Zn	14.9	13.2	9.2	26.5	15.0	13.2
As	0.3	0.3	0.2	0.3	0.2	0.3
Se	0.4	0.2	0.2	0.2	0.2	0.2
Rb	0.6	0.4	0.5	0.3	0.1	0.2
Sr	2.1	1.5	1.8	0.8	0.4	0.8
Cd	0.2	0.1	0.1	0.2	0.1	0.1
Sn	1.3	0.8	0.6	1.6	0.8	0.7
Sb	0.7	0.6	0.4	0.5	0.5	0.4
Ba	5.6	4.9	5.7	3.1	3.4	3.1
La	0.2	0.1	0.2	0.1	0.1	0.1
Ce	0.5	0.3	0.3	0.2	0.1	0.2
Tl	0.1	0.2	0.1	0.1	0.1	0.1
Pb	5.2	4.8	3.8	6.4	4.6	4.6
Bi	0.1	0.2	0.1	0.1	0.2	0.1
Th	0.1	0.1	0.1	0.1	0.1	0.1
U	0.1	0.1	0.1	0.1	0.1	0.1

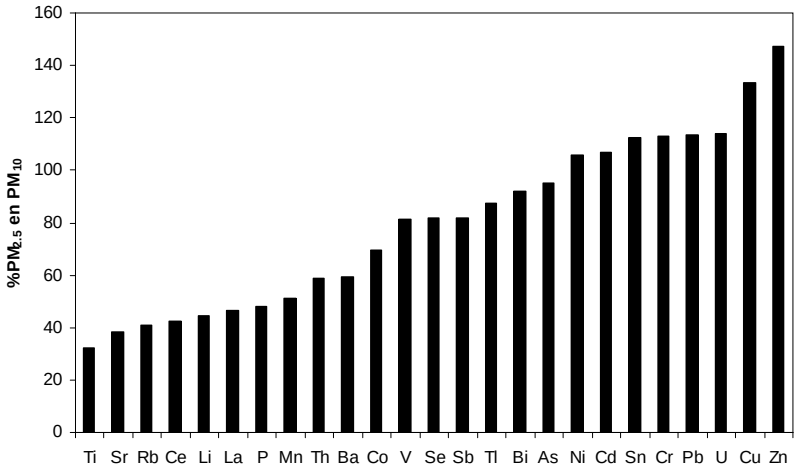

Figure 6.21. Mean $PM_{2.5}/PM_{10}$ ratios for levels of trace elements at Montseny from 2004 to 2006.

Seasonal evolution of PM components at Montseny

PM components at Montseny show a clear seasonal trend. The mean annual cycle of PM components measured at Montseny from 2004 to 2006 in PM_{10} and from 2002 to 2006 in $PM_{2.5}$ is shown in Figure 6.22.

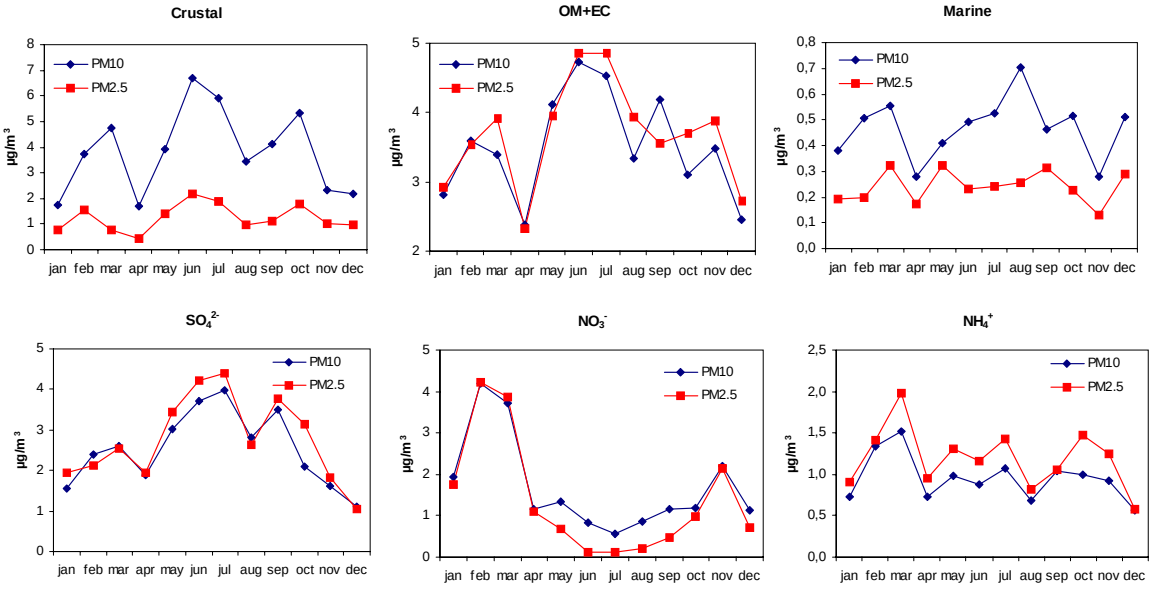

Figure 6.22. Mean annual cycle of the main PM components measured at Montseny from 2004 to 2006 (PM_{10}) and from 2002 to 2006 ($PM_{2.5}$).

The crustal material presents a clear seasonal trend related to the seasonality of African dust outbreaks and similar to the one explained above for Barcelona. During the winter months the levels of crustal components are low. In March there is a maximum, associated to the occurrence of African dust outbreaks during this month. Then, in April the levels are low again due to the higher frequency of precipitations. The levels are high during the summer (June and July) associated to higher soil

resuspension and frequency of African dust outbreaks. In August and September the levels decrease because of the higher precipitation rates. Then, in October the levels increase again, also associated to the occurrence of African dust outbreaks.

The carbonaceous compounds (OM+EC) present the maximum levels during the summer months. These high concentrations are related to the higher biogenic emissions, the regional background anthropogenic pollution and the lower precipitation rates during this period. During the warmer months of the year, the monitoring site is situated inside the boundary layer and it is affected by the regional background pollution of the area. Anthropogenic pollutants are transported from industrial areas in the region affecting mainly OM+EC and SIC levels. In February-March and from September to November the levels are also high. The maximums observed during these months are related to strong local pollution episodes. Pollutants are accumulated in the main valley during some days (there is an industrial area) due to the anticlyclonic atmospheric stability occurring in this period of the year. When the mountain breezes are activated by the solar radiation they carry the pollutants to the monitoring site increasing strongly the levels of some anthropogenic pollutants like carbonaceous compounds and SIA and these sporadic high peaks of pollution contribute to increase the mean levels during these months.

The sea spray levels present high levels in February-March and from June to October, with a maximum in August. These variations could be related to the meteorological scenario and the breezes that carry the sea spray to the monitoring site.

Sulphate levels follow the same seasonal pattern than carbonaceous compounds due to the atmospheric circulation scenarios carrying pollutants to the monitoring site. The high levels during the summer months are also related to the higher oxidation rate of the SO_2 due to the higher photochemical activity except in August, when the levels decrease because of the higher precipitation rates.

Nitrate levels show an inverse relationship with sulphate. The levels are maximum in winter and minimum in summer. This behaviour is due to the thermal instability of ammonium nitrate. The high levels in winter are associated to the strong pollution episodes explained above for carbonaceous compounds.

Ammonia seasonal variation is also associated to the atmospheric transport of pollutants explained above. Ammonia follows a similar trend to nitrate during the winter

months, due to the formation and stability of ammonium nitrate but in the summer the levels do not decrease because of the formation of ammonium sulphate.

6.2.3. Comparison of PM chemical speciation at Barcelona and Montseny

The levels of all the components determined in PM_{10} and $PM_{2.5}$ at Barcelona and Montseny for the period 2004 to 2006 (compared on Tables 6.12 and 6.13 and Figure 6.23) are higher at the urban background site. This increment is more important for components with an anthropic origin.

Table 6.12. Mean levels of PM_{10}, $PM_{2.5}$ and their major components registered at Barcelona and Montseny from 2004 to 2006. ND. Not determined.

2004-2006	Barcelona		Montseny	
µg/m^3	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
µg/m^3	46	32	17	15
OM+EC	10.5	10.2	3.5	3.6
SO_4^{2-}	5.5	4.7	2.7	2.8
NO_3^-	5.2	3.1	1.8	1.4
NH_4^+	1.5	1.8	1.0	1.3
SIC	12.2	9.5	5.5	5.5
Crustal	13.9	5.1	4.4	1.5
Marine	1.9	0.6	0.6	0.2
Unaccounted	7.9	6.4	3.3	3.6

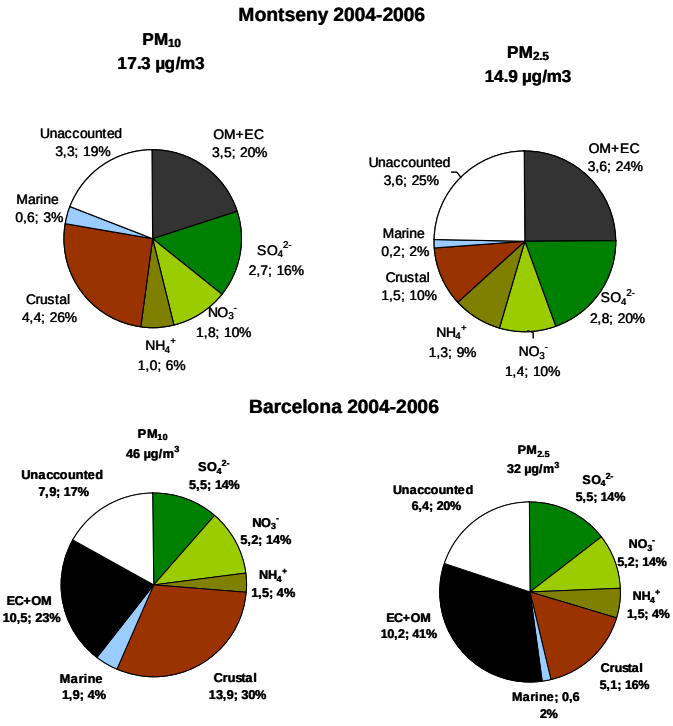

Figure 6.23. Mean annual composition of PM_{10} and $PM_{2.5}$ in Montseny and Barcelona from 2004 to 2006

Table 6.13. Mean levels of trace elements in PM_{10}, $PM_{2.5}$ and PM_1 registered in different sites at Barcelona between 1999 and 2006.

2004-2006	Barcelona		Montseny	
ng/m^3	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
Li	0.6	0.3	0.3	0.1
P	28	4.9	13	6.3
Ti	43	16	21	6.6
V	13	15	3.6	2.9
Cr	5.4	6.8	0.9	1.1
Mn	19	4.7	5.2	2.7
Co	0.4	6.8	0.1	0.1
Ni	5.7	1.7	1.7	1.8
Cu	75	15	6.5	8.2
Zn	102	48	12	18
As	0.9	49	0.3	0.3
Se	0.8	0.7	0.3	0.2
Rb	1.2	0.5	0.5	0.2
Sr	5.8	1.4	1.8	0.7
Cd	0.4	1.3	0.1	0.1
Sn	6.5	1.6	0.9	1.0
Sb	7.0	2.9	0.6	0.5
Ba	25	6.7	5.4	3.2
La	0.4	6.8	0.2	0.1
Ce	0.9	0.3	0.4	0.2
Tl	0.3	0.3	0.1	0.1
Pb	25	5.8	4.6	5.2
Bi	0.7	14	0.1	0.1
Th	0.1	0.3	0.1	0.1
U	0.1	0.1	0.1	0.1

OM+EC levels were clearly higher at the urban background. The higher levels of carbonaceous compounds at Barcelona are mainly attributed to road traffic emissions.

SIC levels are also higher at the urban background, both sulphate and nitrate levels. The high NO_X urban emissions and the SO_2 from industrial emissions produce the formation of nitrates and sulphates with a long mean residence lifetime in the atmosphere. The higher urban sulphate levels are related with SO_2 emissions in Barcelona metropolitan area. Despite the long residence lifetime of these compounds in the atmosphere, Montseny site is located at 700 metres high and sometimes during winter it is situated outside of the boundary layer and consequently is not affected by metropolitan emissions. The difference between SIC levels at the urban and regional site is slightly reduced for $PM_{2.5}$ because the fine compounds present a higher dispersion and affect in the same way more extended geographic areas.

Mineral matter is also higher at the urban site but in this case the difference is more marked for $PM_{2.5}$. A high proportion of mineral matter in PM_{10} and $PM_{2.5}$ at the urban

background site in Barcelona has an anthropic origin and is originated by the resuspension of road dust by traffic and by construction and demolition activities. This fact supports the finding that African mineral dust contribution may have a lower relevance at an annual timescale.

The higher levels of marine aerosol at Barcelona are the result of its proximity to the coast.

The majority of the trace elements analyzed present higher concentrations at the urban than at the regional background. For some metals like Zn, Cu, Pb, V, Ni, Sb, Sn and Cr levels are much higher at the urban background for PM_{10} and $PM_{2.5}$. These elements have an anthropic origin (traffic and industrial emissions) and have a great influence in atmospheric pollution levels at urban areas. For other elements like Ti, P, Sr, Rb, Ce and La, even presenting higher levels in Barcelona, the difference is not so high between the urban and rural site. This fact is attributed to their natural or regional origin.

To conclude, PM_{10} and $PM_{2.5}$ levels recorded at the urban background site in Barcelona that are higher than the levels measured at Montseny regional site are attributed to local emissions, being traffic the source that has a stronger impact on carbonaceous compounds, nitrate and mineral matter levels. Moreover, other disperse punctual sources (small industries, heating, etc.) result in the increase of sulphate, nitrate and carbonaceous compounds. Construction activities have also a great impact on mineral matter concentrations, mainly in the coarse fraction. Therefore, taking into account the relatively low regional background levels we can conclude that an adequate monitoring and control of urban emissions could considerably reduce PM levels registered in Barcelona. The high sulphate, ammonia and nitrate concentrations in Barcelona with respect to the regional site mean that the emission of important precursors are emitted in the urban area, probably from many small and disperse sources.

6.2.4. Influence of African dust outbreaks on PM chemical composition and origin of the crustal load

African dust outbreaks contribute to the mean annual PM levels with1-2 $\mu g/m^3$ in PM_{10} and 0.2-1 $\mu g/m^3$ in $PM_{2.5}$. As stated above, the mean mineral contribution in Barcelona is much higher than this increase in PM levels. It is possible to conclude that the main

fraction of the crustal material has an anthropic origin (road dust resuspension, construction and demolition activities, etc.

The African dust crustal contribution PM would be the difference between the crustal load averages determined by chemical speciation for the annual period and for the days without African dust influence. In Barcelona, for the period 1999-2006 the African contribution to the crustal fraction was between 0.3-2.0 and 0.1-0.7 µg/m^3 for PM_{10} and $PM_{2.5}$ (3-14 and 2-14 % of the mean annual crustal load in the two fractions).

The origin of the crustal load measured in Barcelona can be calculated by comparing the mineral contributions measured at the urban site and at Montseny, a regional background site, 40 km to the north-west of Barcelona. The regional crustal load in PM_{10} and $PM_{2.5}$ measured at Montseny can be broken down into regional soil re-suspension and African dust contribution (unpublished data from the PhD of N. Pérez and J. Pey). The African dust contribution is obtained by calculating the difference between the crustal annual means for all the days and for the days without African dust influence. The mean crustal load calculated for days without African dust outbreaks represents the regional soil contribution. Finally, if the regional mineral load measured at Montseny is subtracted from the bulk crustal levels recorded in Barcelona, the urban mineral increment may be obtained. The results of the above calculations (Figure 6.24) show that in the urban area of Barcelona the African dust, the regional soil re-suspension and the urban increment contributions to the annual mineral load in PM_{10} and $PM_{2.5}$ mean account for about 10, 20 and 70-75 % of the annual crustal load in both cases. Thus, it goes without saying that at least 70-75% of the mineral dust load in both PM_{10} and $PM_{2.5}$ measured at the urban background site in Barcelona is anthropogenic.

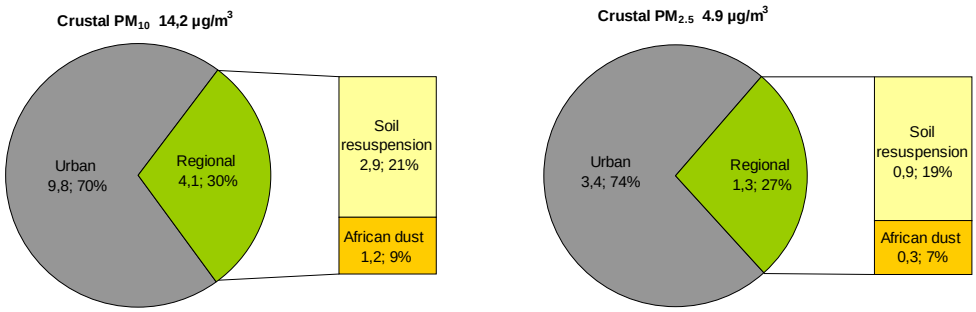

Figure 6.24. Annual mean mineral contribution to PM_{10} and $PM_{2.5}$ at the Barcelona-CSIC site between 2004 and 2006.

6.3. Particle number

6.3.1. Particle number levels at Barcelona

Mean levels and seasonal evolution

The levels of sub-micron particle number concentration in the range 13-800 nm were monitored during November 2003 to December 2004 at the Barcelona urban background site by means of a butanol-based condensation particle counter (TSI CPC 3022A). After that, particle number concentration in the range 3nm-3µm was monitored from June 2005 to June 2007 by means of a water-based condensation particle counter (TSI WCPC 3785).

The mean monthly levels and the mean annual levels for the period of study are presented in table 6.14. The mean levels registered in Barcelona are around 19.000 #/cm^3. These levels are similar to those registered at other urban background sites in Europe (Wichmann et al., 2000).

The monthly means obtained using the water-based WCPC are usually higher than the means obtained with the butanol-based CPC for a given month due to the detection limit, being 13 nm in the case of the butanol CPC and 3 nm for the WCPC. However, this behaviour is not always observed because the levels for a given month vary widely from year to year.

Table. 6.14. Mean monthly levels and annual means of particle number concentration recorded at Barcelona from November 2003 to June 2007.

#/cm^3	2003	2004	2005	2006	2007	Monthly mean
January				13357	17656	15507
February		19657			28822	24240
March		14182			17361	15772
April		11234			22999	17117
May		14436			26702	20569
June				23754	27213	25484
July		16273	21474	21064		19604
August		14661	14573	12894		14043
September		17681	14895	12390		14989
October		19123	14633	30067		21274
November	17845	22209	12901	25846		19700
December			9742	28405		19074
Annual mean		16606	14703	20972	23459	18947

The mean monthly and the mean daily levels from April 2003 to June 2007 are plotted in Figure 6.25. Although monthly levels for a given month may vary widely from year to year (>100%), the higher particle number concentrations are observed in general during two periods during the year: The winter (February and October to December) and the summer (June to July). The high levels recorded during the winter months are the consequence of some important pollution episodes that occur during this period of the year as a consequence of the anticyclonic stagnation of air masses. These situations are characterized by the absence of winds and a minimum thickness of the boundary layer, avoiding the dispersion of pollutants. During the summer the high levels of particle number concentration recorded are attributed to the stronger solar radiation that generates nucleation episodes increasing particle number concentrations during the day. The months registering the minimum levels of particle concentration (March and April) were characterized by a high rate of precipitations and renovation of air masses or also by the reduction of traffic emissions (August and September).

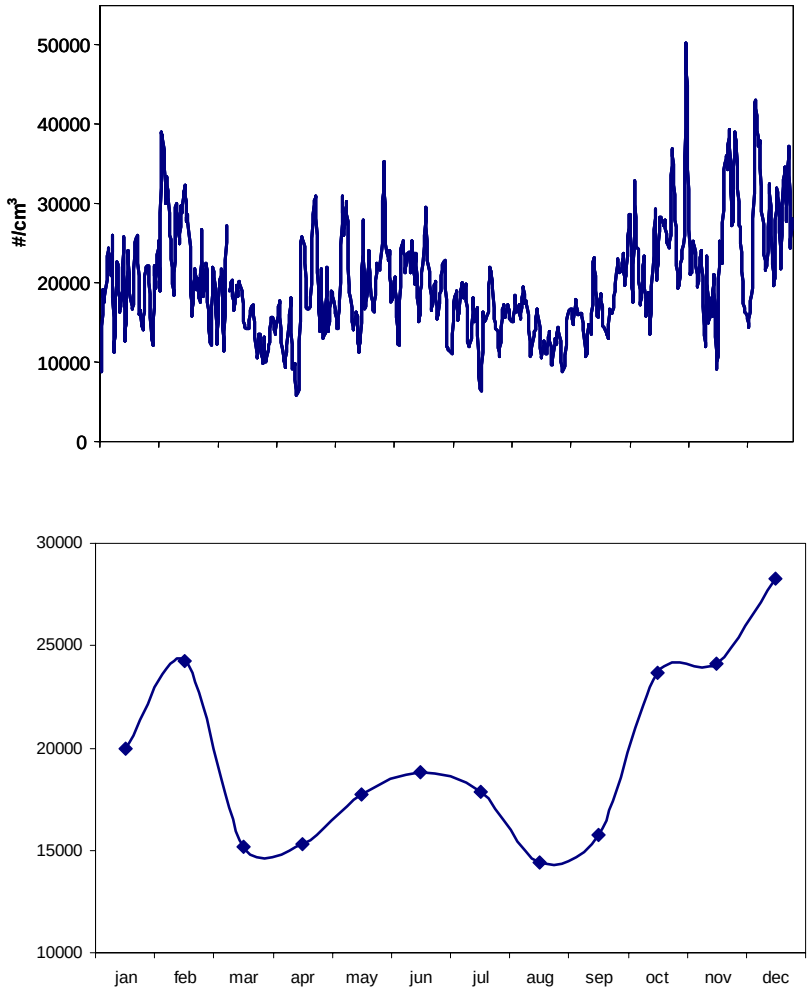

Figure 6.25. Mean annual cycles of daily and monthly particle number concentration levels recorded at Barcelona from April 2003 to June 2007. Data from 2005 needs validation and is not considered for the calculation of the means.

Daily evolution

The study of daily cycles shows that traffic is the major source to particle number levels (Figure 6.26). The maximum levels of particle number are recorded during the traffic peak hours both in the morning (around 7 to 9, local time) and the evening (around 19 to 23, local time). Levels in the evening are high until late hours because of the traffic occurring at night during weekends in the area. During the night hours when the road traffic intensity is reduced the number concentration decreases as a result of coagulation processes and in the morning, when traffic activity starts, the levels increase again. This increase is related to the high number of ultrafine particles emitted directly of formed by nucleation processes from gases emitted by vehicles. After the peak hours, when the emissions are reduced, the fine particles coagulate and condense between them and the number concentration decreases. From 11 to 13 hours (GMT), when the solar radiation is maximum, there is an increase of the levels registered (Figure 6.27) produced by new ultrafine particles formed by photochemical nucleation processes.

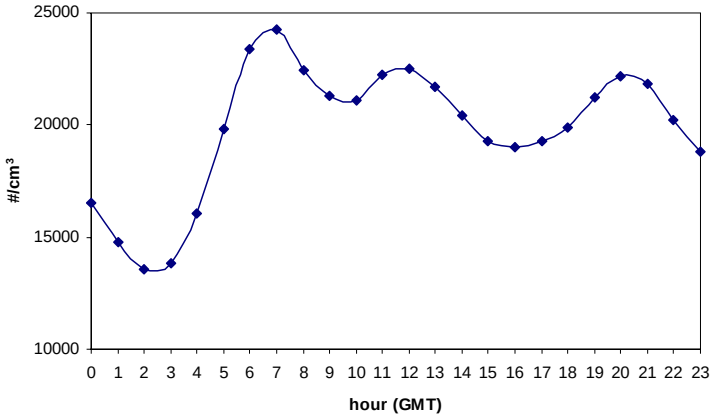

Figure 6.26. Mean daily cycle of particle number concentration levels recorded at Barcelona from July 2005 to June 2007

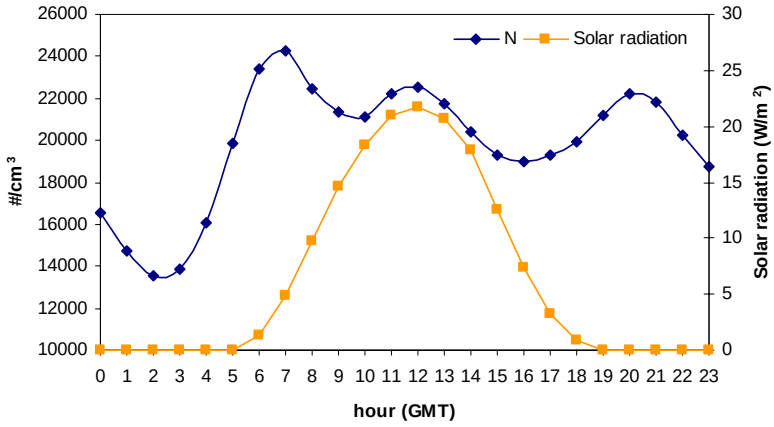

Figure 6.27. Mean daily cycles of particle number concentration levels recorded at Barcelona from July 2005 to June 2007 and simultaneous solar radiation.

6.3.2. PM_X and particle number (N) comparison

Daily cycles

Particle number concentration (N) presents a similar behaviour than PM_{10} $PM_{2.5}$ and PM_1 levels because all these parameters are very influenced by traffic. The levels of N, PM_{10}, $PM_{2.5}$ and PM_1 maximize during both morning and evening traffic peak hours (Figure 6.28) decreasing afterwards by atmospheric dilution processes. During the night hours, when traffic activity is lower, the emissions decrease, being reflected in the levels of N and PM_x.

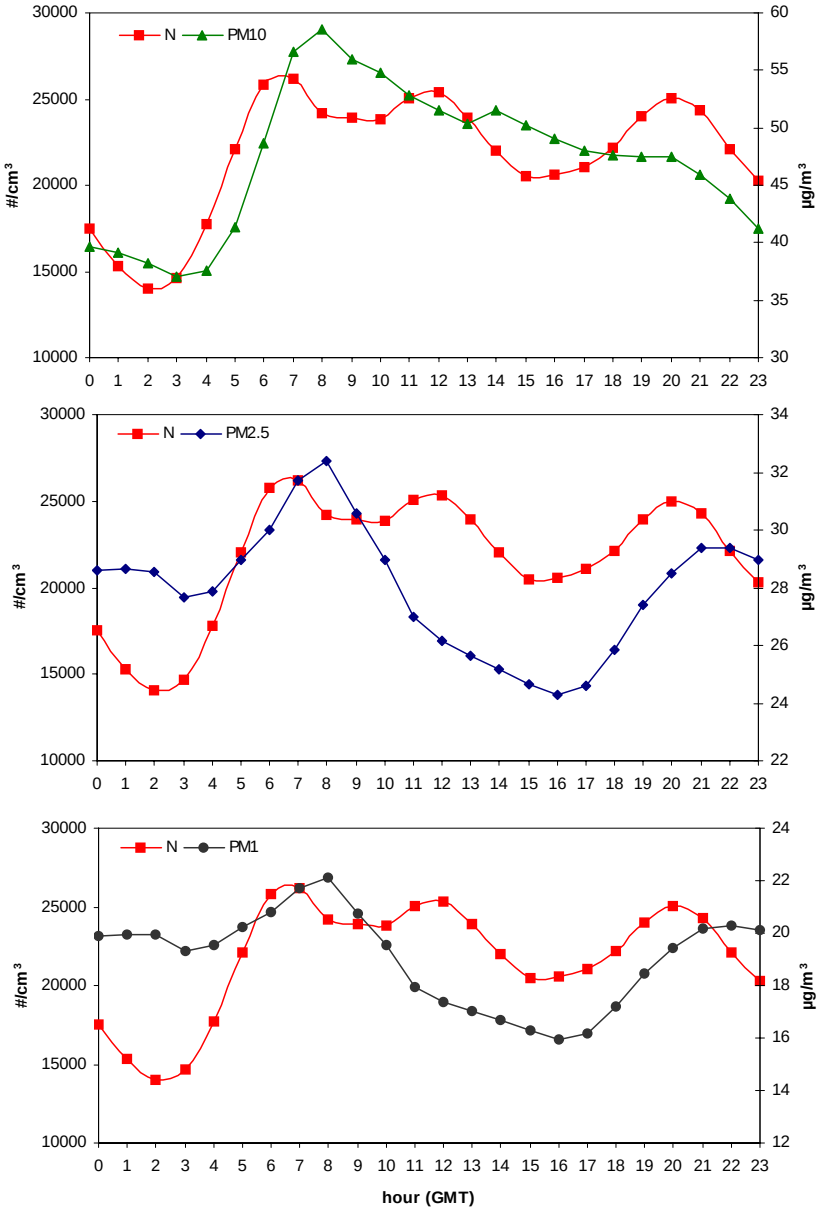

Figure 6.28. Mean daily cycles of particle number concentration levels and simultaneous PM_{10}, $PM_{2.5}$ and PM_1 levels.

PM_{10} levels present a maximum during traffic peak hours as a consequence of road traffic exhaust emissions and the resuspension of road dust. When traffic slows down, the levels decrease because of atmospheric dilution processes and the deposition of coarse particles. $PM_{2.5}$ is composed of accumulation mode particles and mineral dust so it is affected by road traffic emissions but also by road dust resuspension. PM_1 is mainly composed of accumulation mode particles and it is principally affected by road traffic exhaust emissions.

The peaks in PM_{10}, $PM_{2.5}$ and PM_1 levels occur some time after the peak in N levels. N levels fast increase is related to the high number of ultrafine particles emitted directly of formed by nucleation processes from gases emitted by vehicles. Then, the ultrafine particles coagulate and condense between them and the number concentration starts to decrease but the mass concentration increases. PM levels are influenced by direct road resuspension but also by secondary aerosols formed from traffic precursors. Traffic exhaust emission contribution to PM occurs by the condensation/reaction of the aerosol gaseous precursors on the surface of accumulation mode particles forming nitrate, sulphate ammonium and organic matter compounds and that is the reason why the peak mass concentration occurs after the peak number concentration.

The decrease in N and PM_{10} levels during the night is more marked than the decrease in PM_1 and $PM_{2.5}$ levels that remain high. N levels decrease after the peak hours because of coagulation processes and PM_{10} decreases because of the higher deposition rate of the bigger particles. $PM_{2.5}$ and PM_1 levels remain high during the night because their deposition rate is slower and the dilution processes are lower during night time (Viana et al., 2005).

The increase in PM_{10} levels at 14-15 hours (GMT), affecting mainly the coarse grain size, is attributed to dust resuspension from construction activities, as it is coincident with the highest wind speed coming from an area in Barcelona where construction work has been carried out in the last years.

PM_X speciation and particle number seasonal trends

When comparing the mean annual cycles of particle number concentration with the seasonal evolution of some PM_{10} and $PM_{2.5}$ components a similar behaviour is observed for the carbonaceous compounds (OM+EC) and the particle number (Figure 6.29) as they are both very influenced by road traffic. Both OM+EC and particle number present the maximum levels during the winter months, associated to the strong

pollution episodes recorded in this period of the year due to the atmospheric stability. The levels decrease in April, related to the higher precipitation rates, and also in August, because of the lower traffic intensity during this month.

The particle number summer increase attributed to the stronger solar radiation that generates nucleation episodes during the day is also observed for the sulphate, crustal material, and the carbonaceous components. This behaviour, in the case of sulphate is also related to the higher photochemical activity during summer months. The crustal material summer increase depends on other factors such as the soil resulpension and African dust contribution.

The high particle number concentrations observed in February are also observed for nitrate as a result of the strong pollution episodes occurring during this month in Barcelona.

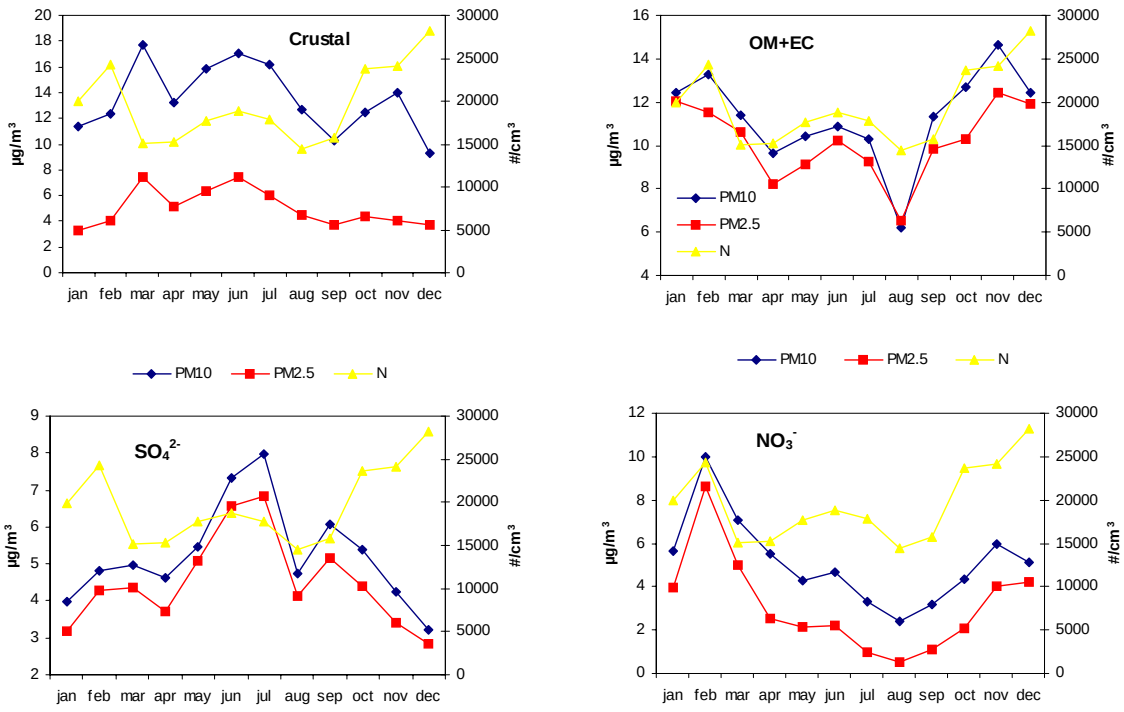

Figure 6.29. Mean annual cycles of particle number concentration and the crustal fraction, OM+EC, sulphate and nitrate in PM_{10} and $PM_{2.5}$ in Barcelona.

7. CONCLUSIONS

The mean annual PM levels measured at Montseny and Barcelona are considered relatively high when compared with the levels obtained in other rural and urban backgrounds around Spain and Europe. We can consider this difference to be associated to anthropogenic emissions as the area of study is very industrialized and populated.

The annual variation of PM levels is highly influenced by the climatology and the frequency of African dust episodes in a year. Temporal changes in anthropogenic emissions, such as road traffic and industrial emissions also influence decisively the mean annual PM levels. In Barcelona although mean annual levels of PM_{10} do not follow a definite trend, those of $PM_{2.5}$ and PM_1 tend to increase from 1999 to 2006, suggesting an anthropogenic origin. Nevertheless the lower PM levels obtained during 2007 suggest that PM variation is due in part to meteorological causes.

Conversely, at the Montseny site PM levels follow a decreasing trend from 2002 to 2007, probably attributed to climatology, but this trend could also be caused by a variation of the anthropogenic regional load because of changes in the industrial emissions in the region.

The concatenation of pollution episodes produced by thermal inversion during the winter favour the increase of PM levels at Barcelona and the decrease of PM levels at Montseny, being isolated for a longer time from the boundary layer.

The contribution of African dust to PM levels depends on the frequency and intensity of African dust episodes in a year. In Barcelona, for the period 1999-2006, between 16-45% of the exceedances of the PM_{10} daily limits levels established by the Air Quality European Union Directive 1999/30/EC were recorded during African dust outbreaks episodes, but not in all cases were the exceedances exclusively caused by the natural contribution. In Montseny the daily limit value was exceeded rarely and almost in all cases can be attributed to the African dust contribution. The frequency and intensity of African dust outbreaks in a year influences decisively the PM mean annual levels at Montseny. The annual levels are also very influenced by the winter pollution episodes occurring in the area.

Results of PM speciation and size partitioning obtained at an urban site in Barcelona (Spain) show that the coarse fraction ($PM_{2.5-10}$) mainly consists of mineral dust (63%), sea spray (10%), and secondary inorganic aerosols (mostly Na, Ca, K, Mg sulphate and nitrate, 20-25%). The $PM_{1-2.5}$ fraction is made up of mineral dust (38%) and secondary inorganic aerosols (27%), with a fraction of carbonaceous matter (24%). The PM_1 fraction mainly comprises OM+EC (46%) with an important fraction of secondary inorganic aerosols (mostly ammonium nitrate and sulphate, 31%) and very minor proportions of mineral dust and sea spray. Thus, PM_1 contains a significantly lower proportion of crustal and marine components and a larger proportion of carbonaceous components than the $PM_{1-2.5}$ and $PM_{2.5-10}$ fractions.

The results show that the strategy of combining PM_{10} and PM_1 monitoring is a good tool for air quality monitoring across Europe. Thus, in PM_1 the dust load is considerably reduced when compared with PM_{10} and $PM_{2.5}$, and the measurement of PM_1 allow us to monitor levels of the same components (mostly carbonaceous and secondary inorganic components) in different scenarios. Simultaneously measured PM_{10} could also provide information on the levels of specific coarse components for a given site, such as mineral dust and sea salt. $PM_{2.5}$ represents an intermediate stage, with varying composition with the monitoring site and it may also be influenced by mineral dust.

In Montseny, the coarse fraction ($PM_{2.5-10}$) was mainly made up of mineral dust (81%), marine aerosol (9%) and nitrate (10%). The carbonaceous material, ammonia and sulphate were found at very low levels in this fraction. $PM_{2.5}$ was a mixture of SIA (40%), carbonaceous material (24%) and mineral dust (10%). The mass of marine aerosol (2%) and that of mineral dust (10%) were reduced in the $PM_{2.5}$ with respect to the PM_{10}. Almost no OM+EC is present in the $PM_{2.5-10}$ fraction. Most sulphate was present in the fine fraction.

The mineral contribution to the annual PM_{10} levels at the Barcelona study site can be broken down into an urban background fraction (65-70%) and a regional background fraction (30%). The regional crustal load can be broken down into the regional soil re-suspension (20-25%) and the African dust contribution (8-16%). Thus, most of the mineral load at this urban site has an anthropogenic origin, although it is accentuated by climate causes as low rainfall, with the consequent scarce washout of the road dust from streets.

The mean levels of particle number concentration registered in Barcelona were around 19.000 #/cm^3. These levels are similar to those registered at other urban background sites in Europe. Particle number concentration measured at the Barcelona urban site is very influenced by road traffic. The study of daily cycles shows that traffic is the major source to particle number levels maximizing during traffic peak hours. PM mass measurements do not allow the study of aerosol processes taking place in the ultrafine particle range as particle number variation is mainly influenced by road traffic and PM levels are influenced also by the contributions of other sources. The measure of both parameters becomes necessary for a detailed study on the impact of the different pollution sources on ambient PM levels and composition.

Particle number levels increase at Barcelona is related to the ultrafine particles emitted directly of formed by nucleation processes from gases emitted by vehicles. When the traffic intensity decreases and the ultrafine particles coagulate and condense between them, the number concentration decreases but the mass concentration increases. At noon, when the solar radiation is maximum, there is an increase of the levels of particle number registered produced by new ultrafine particles formed by photochemical nucleation processes.

PM levels are influenced by direct road resuspension but also by secondary aerosols formed from traffic precursors. Traffic exhaust emission contribution to PM occurs by the condensation/reaction of the aerosol gaseous precursors on the surface of accumulation mode particles forming nitrate, sulphate ammonium and organic matter compounds.

8. FUTURE WORK

To reach the final objectives of the PhD in progress, the following tasks have to be accomplished:

- To complete the interpretation of PM levels and speciation measured at Barcelona and Montseny until the end of 2007.
- To complete the interpretation of the results on particle number concentration measured at Barcelona until the end of 2007.
- To analyze the data on PM levels and speciation measured at two more monitoring sites located in the Canary Islands: Santa Cruz de Tenerife (an urban background site) and Izaña (a free-troposphere remote monitoring site with no impact of anthropogenic emissions). The monitoring of PM levels and speciation at these two sites, at a lower distance from Northern Africa than the Barcelona area and thus with a higher impact of African dust outbreaks, has been carried out since 2002, and the interpretation of the PM series and their comparison with the results obtained in Barcelona and Montseny will be useful to characterize the natural and anthropogenic mineral dust behaviour and its influence on PM levels and speciation in the Iberian Peninsula.
- To carry out the source apportionment analysis of the data obtained by receptor modelling techniques (principal component analysis, cluster analysis, etc.) for all the monitoring sites, with the objective to identify and quantify the different sources and their contribution to PM levels at each of the monitoring sites.
- Publication of the results obtained in scientific journals and conferences.

9. PUBLICATIONS, CONTRIBUTIONS TO CONFERENCES AND WORKSHOPS AND FORMATION COURSES

9.1 Publications

- **Pérez N.,** Querol X., Alastuey A., Pey J. Partitioning of major and trace components in PM_{10}-$PM_{2.5}$-PM_1 at an urban site. Atmospheric Environment (submitted, 2007).
- Querol X., Pey J., Minguillón M.C., **Pérez N.,** Alastuey A., Viana M., Moreno T., Bernabé R.M., Blanco S., Cárdenas B., Vega E., Sosa G., Escalona S., Ruiz H., Artíñano B. PM speciation and sources in Mexico during the MILAGRO-2006 Campaign. Atmospheric Chemistry and Physics Discussions (submitted, 2007).
- Sunyer J., Jacquemin B., Querol X., Viana M., González-Cabré M., Valero N., Baldasano J.M., Pérez C., Jiménez P., Jorba O., Alastuey A., Castillo S., Escudero M., Moreno T., **Pérez N.**, Pey J., Calzada N., Gracia J., Cots N., Guinart X., Hernandez I., Pérez L. (2006). Contaminación del aire por partículas y salud en Barcelona. Revisión de estudios científicos publicados con datos de la ciudad de Barcelona Consorci Sanitari de Barcelona. Agència de Salut Pública.
- Escudero M., Querol X, Pey J, Alastuey A, **Pérez N.**, Ferreira F, Alonso S, Rodriguez S, Cuevas E. (2007). A methodology for the quantification of the net African dust load in air quality monitoring networks. Technical note. Atmospheric Environment 41, 5516-5524.

9.2 Contributions to conferences and workshops

- Querol X., Minguillón M.C., Pey J., **Pérez N.**, Alastuey A., Moreno T., Bernabé R.M., Blanco S., Cárdenas B. Speciation of particulate matter in the Mexico City Metropolitan Area during MILAGRO campaign. 1st MILAGRO Science Meeting. Colorado, USA. 23-25 October 2006. Poster presentation.
- Querol X, Pey J, Minguillon MC, **Pérez N**, Alastuey A, Moreno T, Bernabe RM, Blanco S, Cardenas B. Levels, composition and sources of PM in the Mexico city metropolitan area during the MILAGRO campaign. AGU Joint Assembly 2007. Acapulco, Mexico, 21-25 Mayo 2007. Poster Presentation.
- González R, Márquez C, Bernabé R, Snyder DC, Rutter AP., Minguillón MC, **Pérez N**, Pey J, Alverdin L, Reyes E, Miranda L, Miranda J, Moreno T, Blanco

S, De la Rosa A, Solórzano G, Alastuey A, Schauer J, Querol X, de Foy B, Molina LT, Cárdenas B. Measurements of Total Gaseous and Particulate Mercury in Mexico City During the MCMA-2006/MILAGRO Campaign. AGU Joint Assembly 2007. Acapulco, Mexico, 21-25 Mayo 2007. Poster Presentation.

- Querol, X., Minguillón, M.C., Pey, J., **Pérez, N.,** Alastuey, A., Moreno, T., Bernabé, R.M., Blanco, S. & Cardenas. B. Levels and composition of PM in the Mexico City metropolitan area: the MILAGRO campaign. EGU General Assembly 2007, Viena 16-19 Abril 2007. Geophysical Research Abstracts, Vol. 9, 09357, 2007.
- **Pérez N**, Pey, J , Alastuey A, Querol X, Castillo S, Escudero M. Origin of mineral dust in PM levels at an urban and a regional site in North-Eastern Spain. African dust outbreak impact. Poster. Primera Reunión Española de Ciencia y Tecnología de Aerosoles, RECTA 2007. Madrid, 5-6 July 2007. Poster presentation.
- **Pérez N**, Pey, J , Alastuey A, Querol X, Castillo S, Escudero M. Influence of african dust outbreaks on levels and composition of particulate matter in an urban background in Barcelona, Spain. IAMAS Mineral Dust Aerosol Symposium. IUGG XXIV General Assembly "Earth: our changing planet". Perugia, 9-12 July 2007. Poster presentation.
- Aas W., Alfarra M.R., Bieber E., Ceburnis D., Ellermann T., Ferm M., Frölich M., Gehrig R., Hansson H.C., Kiss G., Makkonen U., Mihalopoulos N., Nemitz E., Otjes R., **Pérez N.**, Perrino C., Putaud J.P., Spindler G., Tsyro S., Vana M., and Yttri K.E. (2007).Intensive measurements and modelling of size segregated chemical composition of aerosols in June 2006 and January 2007 in EMEP. European Aerosol Conference 2007, Salzburg, Abstract T01A053.
- Aas W., Fölich M., Gehrig R. **Pérez N.,** Perrino C., Putaud J.P., Spindler G., Tsyro S., Yttri K.E. (2007). Size segregated chemical composition of aerosols, EMEP intensive measurements 06/07. Poster presentation.

9.3 Assistance to scientific formation courses

- PhD courses in Environmental Sciences at the *Institut de Ciència i Tecnologia Ambientals*. *Universitat Autònoma de Barcelona*. Barcelona, 2005-2006.
- Formation course: '*Measurement of atmospheric aerosols: Aerosol Physics, sampling and measurement techniques*'. Hyytiälä, Finland (10 to 20 May 2006).

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